

CHRISTIAN FREDERICK SCHÖNBEIN  
Discoverer of the Cellulose Nitrates.



# NITROCELLULOSE INDUSTRY

A COMPENDIUM OF THE HISTORY, CHEMISTRY, MANUFACTURE,  
COMMERCIAL APPLICATION AND ANALYSIS OF NITRATES,  
ACETATES AND XANTHATES OF CELLULOSE  
AS APPLIED TO THE PEACEFUL ARTS

WITH A CHAPTER ON

GUN COTTON, SMOKELESS POWDER AND EXPLOSIVE  
CELLULOSE NITRATES

BY

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high solvent power and low moisture absorption during evaporation, thus reducing the tendency toward clouding and fogging of the films.<sup>1</sup>

The statement is found in the literature that all forms of cellulose nitrate are soluble in acetone and acetic ether, and a rough method of estimating unchanged cellulose has been suggested by dissolving the cellulose nitrate in one of these solvents, the insoluble portion being cellulose. In many examinations of ethyl acetate-insoluble residues from cotton nitration, the author has yet to find one free from nitrogen, even after the acetate has been left in contact with the nitrated cotton for periods of as long as two weeks, with daily change of solvent. The percentage of nitrogen as calculated on the sample dried at 100° has varied from 0.2–4.7, thus indicating the presence of nitrogen-containing bodies in nitrocotton, insoluble in ethyl acetate. The anomalous results in solubility reported by different investigators render accurate generalizations impossible at the present time. A nitrocotton of 12.5% nitrogen may be practically insoluble in ether-alcohol or may entirely dissolve to a clear and fluid solution. The curious observation has been made and substantiated that a nitrocotton solution in ether-alcohol, amyl acetate, or acetone, decreases in viscosity upon standing if the solution be slightly acid. This fact is made use of in the artificial silk industry, where, in Germany, Lehner has obtained patent protection for the expression "acid-moistened collodion." If the nitration produces a pyroxylin of higher viscosity than desirable, the solution in ether-alcohol or amyl acetate is made faintly acid—usually by the addition of 0.2% acetic acid—and exposed to the light. The viscosity gradually diminishes, and when it reaches the desired point the solution is either used in the acid state or carefully neutralized by alcoholic sodium hydroxide, the sodium acetate formed being readily soluble and hence the clearness of the solution unimpaired. Although the viscosity of cellulose nitrate solutions bears no direct relation to the nitrogen content, still it reaches its maximum with the highest percentage of nitrogen. The presence of traces of acid in amyl acetate-pyroxylin solutions does not decrease the viscosity as quickly or to as great an extent as the same pyroxylin and same percentage of acid dissolved in ether-alcohol. The viscosity of solutions sinks with increase of water content in the nitrating mixture, and the yield is correspondingly lowered. Nitration of the same cotton at 20° for eight hours, at 40° for two hours, or

1. In fact Hönig and Schubert, *Mon. Sci.*, 1864, 6, 708; 1865, 7, 455, and Blondeau de Carolles, *J. pr. Chem.*, 1865, (2), 32, 427, have described water-soluble, sulphuric acid cellulose esters, which upon treatment with alcohol regenerate bodies of the nature of cellulose, partly soluble and partly insoluble in water.



at 60° for fifteen to twenty minutes, can be made to produce a nitro-cotton of substantially the same solubility, but not necessarily of same viscosity.

The above generalizations include most of the observations of direct value of these two constants as affected by nitration.

**Stability of the Cellulose Nitrates.** Among the characteristics which distinguish the cellulose nitrates the property of stability has been most exhaustively investigated. Due to the numerous and fatal explosions which have occurred from time to time in factories where these esters are manufactured, the volume of research on this subject has been considerable.<sup>1</sup> Although numerous qualitative and quantitative observations have been made as to the causes underlying the decomposition of these esters, a great many points are still open to experimentation. From the mass of experimental data accumulated, it appears that the factors which cause instability in cellulose nitrates may be comprised within the following classification:

(1) The formation of sulphuric esters in the nitrating process, not entirely eliminated in the subsequent washings. Cross, Bevan, and Jenks<sup>2</sup> have obtained sufficient results to establish the fact that sulphuric acid does take part in the ester reaction, in addition to its well-known function of dehydration. Hake and Lewis,<sup>3</sup> in investigations on the formation of these sulphuric esters in the nitrating process, have found that sulphuric acid is combined in all products of nitration where used in the nitrating mixture, their formation being due to delayed nitration, with partial solution or gelatinization of the cellulose by sulphuric acid and subsequent nitration. Also that the proportion of sulphuric acid is determined by the ratio of sulphuric to nitric acids in the nitrating bath.<sup>4</sup> They found that in nitration with nitric acid alone, and subsequent precipitation with

1. For bibliography see Silberrad and Farmer, *J.C.S.*, 1906, **90**, 1172; also Maurey, Béchamp, Kuhlmann, Pelouze, and de Luca, *C.R.*, 1818, **28**, 343; 1853, **37**, 134; 1856, **42**, 676; 1864, **59**, 363, 487; Heussermann, *Ber.*, 1903, **36**, 3956; 1904, **37**, 1624.

2. *Ber.*, 1901, **34**, 2496; cf. O.W. Willeox, *J.A.C.S.*, 1908, **30**, 271; for "Ignition Points of Nitrocellulose and Smokeless Powders," see G. Finzi, *Gazz. Chim. Ital.*, 1909, **39**, (1), 549; abstr. *J.S.C.I.*, 1909, **28**, 676.

3. *J.S.C.I.*, 1905, **24**, 374, 914; cf. Hake and Bell, *J.S.C.I.*, 1909, **28**, 457; Cross and Bevan, "Cellulose," 1900-1905, 53; Briggs, *Ber.*, 1905, **38**, 358; see "Action of Sulphuric and Nitric Acids in the Nitration of Cellulose," *J.S.C.I.*, 1909, **28**, 823.

4. There is no doubt that sulphuric acid plays an important part in the stability of cellulose nitrate, where a mixture of nitric and sulphuric acids is used for nitrating. There is much evidence to show that with nitric acid alone a purer and more stable product is formed. In many receipts for the manufacture of collodion for photographic use it is recommended that no sulphuric acid be used. Where the sulphuric acid attacks and dissolves the cellulose, the initial product may be regarded as cellulose sulphuric acid, but a rapid molecular rearrangement takes place and a series of sulphates result.

sulphuric acid, no sulphuric acid was combined with the nitrocotton. A ratio between sulphur content and stability, other factors being equal, is claimed. The amount of combined sulphates may be decreased by subjecting the nitrated cotton to the vapors of various solvents, especially glacially acetic acid.

(2) The presence of hydro- and oxy-cellulose in the cellulose before nitration. It is generally conceded that undue bleaching of cotton or other treatment which partially alters the cellulose fiber results in the formation of a nitrate of diminished stability. These bodies have ill-defined characteristics, but it has been repeatedly verified that a pure cellulose, when nitrated, forms a more stable ester than a cellulose which has been altered in chemical structure by bleaching or other chemically harsh treatment. The best method as yet found for removing these altered cellulose nitrates is continued washing, without neutralization by alkali.<sup>1</sup>

(3) Traces of free nitrating acids, only found in products of faulty methods of washing, undoubtedly result in instability, as indicated by the low heat tests. This defect can be removed by continued washing without alkali.

(4) Vegetable wax and resinous bodies associated with cotton in the raw state, and incompletely removed during the processes preparatory to nitration. Where scouring of the cotton has been imperfect, or waste cotton is employed which has been incompletely purified from oil, grease and extraneous matter, it is found that the stability of the resulting nitrate is low. There has been no well-defined process worked out to remove these bodies after nitration, in order to bring the cellulose nitrate to the required stable state.

(5) The presence of molds or other micro-organisms. The fact noted<sup>2</sup> that cellulose nitrates sometimes contract mold, and the judgment of Sy<sup>3</sup> that denitrifying bacteria might start a decom-

1. The work of Leo Vignon (C.R., June 6, 1898; Sept. 10, 17, 1900) on the formation of oxy- and hydro-cellulose shows plainly that cotton and cotton waste may, by the nature of the treatment to which they are subjected, be partly transformed into oxycellulose, which gives an unstable nitrate, and into hydrocellulose, which has a different rate of nitration than ordinary cellulose. Cross and Luck (J.S.C.I., 1900, 19, 642; E.P. 5286, 1898) remove such foreign substances by means of acetone so diluted with water that it does not dissolve the higher nitrates. Will and Lenzl (Ber., 1898, 31, 68) have examined many nitrated carbohydrates for stability, in general finding them unstable.

2. O. Guttman, "Manufacture of Explosives," 1905, 2, 49; cf. J.S.C.I., 1897, 16, 283; 1898, 17, 1180; 1899, 18, 174, 857; 1901, 20, 8, 609; 1902, 21, 819, 1470; 1903, 22, 511, 924, 1208; 1904, 23, 953, 1903; 1905, 24, 148, 347.

3. Jour. U.S. Artill., Sept.-Oct., 1903; T. Bokorny (Chem. Zeit., 1896, 20, 985) found that cellulose trinitrate will serve as a food supply for molds, if suspended in distilled water containing the requisite amount of mineral matter, and placed in the dark. However, no growth was observed if mineral matter be absent.

position, led Malenkovic<sup>1</sup> to study the problem experimentally, from which he concluded that neither cellulose nitrates or glycerol nitrates are directly decomposed by mold, but that the cellulose nitrates when placed in contact with organic matter are superficially decomposed. It appears, therefore, that danger of instability from mold is, at least, a remote one. It is to be noted that to prevent molding, small amounts of mercuric chloride are added to the cotton. Mercury possesses the property of combining with cellulose in a manner which causes the mercury to remain, even after repeated washings. Such nitrocotton-containing mercury gives a factitious higher stability test.

(6) Other compounds associated with the nitrocotton, nitrosaccharoses, pectins, and other vaguely characterized bodies. They cause instability, and are difficultly removable by washing, by digestion with cold alkaline solutions, or by extracting with ether, alcohol, or benzene. All are, however, partially, at least, soluble in acetone, pyridine, and ethyl acetate. They are neutral to test paper, but become acid upon boiling or otherwise heating.<sup>2</sup> They often combine with metallic oxides, as lead and zinc, and these combinations are much more stable.<sup>3</sup> It was formerly considered that the lower nitrated bodies were sources of instability, but the now generally accepted fact is that the lower nitrated celluloses are of increased stability. The presence of unusually large amounts of nitrogen tetroxide does not decrease the stability of the nitrated cotton. Bergmann and Junk<sup>4</sup> found that when an unstable ester was extracted with alcohol

1. Rev. d'Art, 1908, **71**, 261; Mitteil u. Gegenstände J. Artill. u. Geniew., 1907, 509; abst. J.S.C.I., 1907, **26**, 1295. M. Jacque, Z. ges. Schiess- Sprengstoffw., 1910, **5**, 81, reports instances of blocks of compressed guncotton (containing 15% of water) showing very marked growths of micro-organisms, but in no case was the nitrogen content or stability of the nitrocellulose affected. Attempts to cultivate the spores of *Aspergillus niger* and *Mycetozoa* in nitroglycerol and ethyl and amyl nitrates were not successful. It is pointed out that the *algae* and aquatic plants produce organic salts, especially oxalates, during decomposition, and that traces of these organic salts would adversely affect the heat test of guncotton and nitroglycerin. In support of this view the author mentions that in 1907 one of the large dynamite factories in Mexico experienced great difficulty in obtaining heat tests up to their standard of fifteen minutes at 76°. Investigation showed that the cause of the trouble lay in the fact that the water reservoirs and channels had considerable quantities of vegetable growths in them, and when this was cleared away the heat tests of the guncotton and nitroglycerin returned to their normal figures.

2. Ulmic bodies, which are closely related to the higher members of the acetic series, may also influence the stability of a not thoroughly purified cellulose nitrate. Girard states (Ann. Chim. Phys., 1881, **24**, 337) that when hydrocellulose is heated above 80° it is converted into ulmic bodies possessing an acid reaction. A. L. Stern (J.C.S., 1904, **85**, 336) doubts the accuracy of this statement, but says that when care is taken to remove all traces of acids no such bodies are formed, but easily form with traces of acid. See also Hake and Lewis, J.S.C.I., 1905, **24**, 378.

3. This method has been patented, U.S.P. 647420, 1900; E.P. 18868, 1898.

4. Z. ang. Chem., 1904, **17**, 982, 1018, 1074.

for some time, a stable compound was always produced. J. C. Thomas<sup>1</sup> has found that for the purpose of neutralizing any acid formed after drying, some manufacturers use a small amount of chalk, which probably exerts a sufficiently pronounced saponifying effect to account for the decreased stability. Will has shown<sup>2</sup> that in cellulose nitrates the rate at which nitrogen splits off increases with the percentage of water in the nitrating acids, and also as the ratio of sulphuric to nitric acid increases. That the longer cellulose nitrate is boiled with calcium carbonate, the greater the tendency to decomposition; the percentage of nitrogen is without influence on the stability; boiled nitrocellulose, subsequently washed, gives the iodide reaction immediately, when washed only half an hour; a lower nitrated cellulose is more stable than a higher one; and addition of alkali is worthless, if not detrimental.

Silberrad and Farmer<sup>3</sup> have made exhaustive investigations on the gradual deterioration of cellulose nitrates on storage. They found that nitric peroxide is liberated, a gradual but continuous loss in weight occurs; the percentage of nitrogen decreases; the ether-alcohol soluble matter increases, while the acetone residue shows a slight tendency to increase. It has been shown<sup>4</sup> that the majority of the decomposition products of the cellulose nitrates are soluble in water, and that the water-soluble matter increases on storage. Their results showed conclusively that at any given temperature the rate of deterioration is much greater in a moist atmosphere than in the absence of water, the reason probably being that the hydrolytic decomposition of the nitric esters requires the presence of water. Stability of nitrocotton as regards atmospheric and climatic influences has still to be conclusively tested. It seems to be very difficult, if not impossible, to obtain satisfactory and stable cellulose nitrates by direct nitration of wood pulp.

It has been found<sup>5</sup> that the rate of decomposition of cellulose nitrates cannot be experimentally established for temperatures below

1. Zeit. ang. Chem., 1898, **11**, 1003; 1907, **20**, 1113; abst. J.S.C.I., 1898, **17**, 1130; 1903, **22**, 924; 1904, **23**, 953.

2. Gummitzg., Celluloid Supp., 1896, **5**, 21.

3. J.S.C.I., 1906, **25**, 961, cf. Abel, Phil. Trans., 1867, **157**, 181; Spica, Atti del Reale, Ist Veneto, 1899, **58**, 289; also "Causes of Decomposition of Nitrocellulose," M. Jacque, Z. ges. Schiess- u. Sprengstoffw., 1906, **1**, 395.

4. Silberrad and Farmer, J.C.S., 1896, **69**, 1184. They found present in the aqueous extract ethyl nitrite and nitrate, nitrous and nitric acids, ethyl alcohol, ammonia, formic, acetic, butyric, dihydroxybutyric, oxalic, tartaric, isosaccharinic, and hydroxypyruvic acids. Also carbohydrates by the fermentation test.

5. A. V. Saposhnikov, J. Russ. Phys. Chem. Soc., 1905, **37**, 280; 1906, **38**, 1186; 1907, **39**, 1186; Mem. des Poudres et Saltpêtres, 1907-1908, **14**, 42, and M. Borissow, J. Russ. Phys. Chem. Soc., 1904, **36**, 836; Chem. Centr. 1904, **2**, 1030.

125° nor above 155°; at the former the reaction is too slow, at the higher it comes too near the explosion point.<sup>1 2</sup>

**Starch Nitrate.** Since 1833, when Braconnet produced "xyloidine" by the action of nitric acid upon starch, numerous attempts have been made to prepare this body in a pure and stable state, but until recently it has been impossible to produce this nitrate on a manufacturing scale, due apparently to the extensive washing required to eliminate traces of acid, and the deficient stability of the finished product.<sup>3</sup> The process of W. Schüekler,<sup>4</sup> which is essentially the method at present employed, consists in first drying the starch at 100° in order to eliminate all traces of moisture, and after grinding to an impalpable powder, immersing in nitric acid of 1.5 sp.gr. at 20–25°. After thorough and repeated agitation in the nitrating fluid, the starch is transferred to another receptacle and covered with sulphuric acid of 1.84 sp.gr. The starch nitrate so produced is washed free from acid, pressed in cakes, and dried at a low temperature. Many inventors made unessential modifications of this process, but it was not until 1904 that A. Hough<sup>5</sup> succeeded in sufficiently stabilizing the refined nitrate to admit of its technical use without danger.<sup>6</sup> He produces a nitrostarch containing 16.38% N, using oleum to main-

1. For temperatures between 125–140° and 145–155° the relation of reaction velocity to temperature can be expressed by the following equations respectively:  $\frac{(dv)}{(dt)_{\max}} = -24.6 + 0.201t$ , and  $\frac{(dv)}{(dt)_{\max}} = -136.5 + 0.985t$ . The relation of velocity to temperature therefore within each of these intervals is represented by a straight line.

2. According to F. I. Du Pont and F. Sparre (U.S.P. 836704, 1906; abst. J.S.C.I., 1907, 28, 553) a cellulose nitrate may be stabilized by removing by means of solvents a portion of the unstable bodies. Their process consists in agitating with nitrocellulose, suspended in a liquid in which it is insoluble, an emulsion of a solvent of nitrocellulose diluted by a substance which is insoluble in the liquid in which the nitrocellulose is suspended, and which is not a solvent of nitrocellulose, but is soluble in the nitrocellulose solvent. As an example: 1 part of nitrocellulose suspended in 8 parts of water is agitated with 1 part of amyl acetate diluted by 0.25 part of a liquid such as amyl alcohol or benzine. See U.S.P. 503583, 1893; E.P. 15865, 1893, for similar stabilizing process.

3. By means of the process introduced by the "Actiengesellschaft Dynamit Nobel."

4. E.P. 11665, 1889; 14625, 1890.

5. U.S.P. 751076, 1904; E.P. 21171, 1902; 12627, 1904; D.R.P. 172549, 1906; abst. J.S.C.I., 1902, 21, 1471; 1904, 23, 385; 1905, 24, 691.

6. His method was to inject dry, finely powdered maize starch below the surface of a mixture containing 3 parts nitric acid, 2 parts sulphuric acid (98%) and sufficient Nordhausen fuming sulphuric acid (containing 40% SO<sub>3</sub>) to "bring the nitric and sulphuric acids to 100% concentration," and leave an excess of 2–3% free SO<sub>3</sub>. A further quantity of Nordhausen acid is added during the process to maintain the strength of the nitrating liquid. The temperature of nitration varied between the limits 45–50° F. The starch after nitration is separated by filtration, freed from lower nitro-derivatives by treatment with hot dilute ammonia, and dried. The finished product is described as an orange-yellow powder, readily soluble in ether-alcohol. Nitrogen, 16.5%.

tain about 2% free  $\text{SO}_3$  in the acid mixture during nitration. Recently E. Berl and R. Büttler,<sup>1</sup> in repeating Hough's work, were unable to confirm his results of high nitrogen content. The next year F. Holmes assigned to the Eastern Dynamite Company, of Wilmington, Del., a process by means of which the nitrate was stabilized by boiling with calcium carbonate,<sup>2</sup> and continuing the purification by dissolving the nitrated starch on a mixture of alcohol and acetone.<sup>3</sup> He found the nitrate to be left in a stable state upon distilling off the

1. Z. ges. Schiess- u. Sprengstoffw., 1910, 5, 82. They injected 10 gm. of starch by means of compressed air into 30 gm. of a cooled acid mixture consisting of equal proportions of nitric acid and sulphuric acid, and with sulphur trioxide in excess. The starch nitrate was stabilized by boiling with a solution of ammonia, and was afterwards washed with water. The following table gives the results obtained with starches of different origins.

Starch.	Nitrogen. Per Cent.	Ignition Point. °C.	Relative Viscosity (2 Per Cent. Acetone Solution).
Maize.....	13.23	121	1.86
Potato.....	13.44	120	3.78
Rice.....	12.86	135	1.60
Soluble.....	13.35	120	1.35
Potato.....	13.44	...	2.66
Cellulose nitrate.....	13.40	...	1.05

The viscosity figures refer to acetone as unity. All the starch nitrates were insoluble in alcohol. In a mixture of ether and alcohol the nitrates prepared from rice and soluble starch were freely soluble, while the others were only partially soluble. The normal moisture content of the nitrate prepared from potato starch was 6.57%. A comparison was also made between the nitration of cellulose and potato starch with an acid consisting of sulphuric acid (40.84%), nitric acid (55.33%), and sulphur trioxide (3.83%). The proportion of acid to carbohydrate was 50 to 1.

2. U.S.P. 779421, 779422, 1905.

3. Holmes in describing his process says: "The starch is mixed with concentrated nitric and sulphuric acids, preferably in the proportion of 25 parts starch to 100 parts of mixed nitric and sulphuric acids in the following proportion: nitric acid 32.5%, sulphuric acid 64.5%, water 3%, although these limits may be varied somewhat and still produce a satisfactory product. After separation from the acids, the nitrated starch, which is then in an unstable condition due to impurities, is mixed with alcohol and a reagent which has a lower evaporating point than the alcohol, and which reagent alone or in the presence of alcohol, will dissolve the nitrated starch.

"As the reagent above mentioned, I have used acetone or ether, both of which have a lower evaporating point than alcohol. The acetone alone will dissolve the nitrated starch. The ether alone will not dissolve all the nitrated starch, but in conjunction with the alcohol will dissolve substantially all. Both acetone and ether have a lower evaporating point than alcohol. Acetone is preferable because a higher nitrated product is obtained than where ether or ether and alcohol is used. With acetone, the lower nitrates remain in the solution, while when ether is used, some of the lower nitrates are subsequently precipitated. Approximately 1 part nitrated starch to 1 part acetone or ether and 2 parts alcohol is preferred. After the nitrated starch has been dissolved, the acetone or ether is evaporated off, leaving the former in suspension in the alcohol. Irrespective of which solvent is used, those impurities which tend to produce instability in the starch will remain in solution in the alcohol while the stable nitrated starch, being insoluble, is precipitated out, and dried, after filtration."

acetone.<sup>1</sup> The next year<sup>2</sup> a process was published for rendering the purification less tedious, by separating the product in a flaky mass, which could be readily washed.

The original product prepared by Braconnet was claimed to possess the formula  $C_6H_8O_3(NO_3)_2$ , but O. Mulhäuser,<sup>3</sup> as the result of an extended series of researches, was able to prepare and separate two bodies of the following definite composition, viz:

- |     |                     |
|-----|---------------------|
| (a) | $C_6H_7O_2(NO_3)_4$ |
| (b) | $C_6H_7O_4(NO_3)_3$ |

or doubling the molecule of starch in order to give the expression whole numbers; and adding a product of 11.1% total nitrogen obtained:

Tetranitrostarch	$C_{12}H_{16}O_6(ONO_2)_4$	... nitrogen	11.11%
Pentanitrostarch	$C_{12}H_{15}O_5(ONO_2)_5$	...	" 12.75%
Hexanitrostarch	$C_{12}H_{14}O_4(ONO_2)_6$	...	" 14.14%

That not nitro compounds, but true esters of starch are formed was proven by the fact that the substances separate nitric acid upon treatment with sulphuric acid, while nitric oxide and soluble starch are both regenerated upon treatment with aqueous ferrous chloride. Furthermore, upon shaking a sample with sulphuric acid over mercury, all the N is split off as NO. Mulhäuser has described these bodies in detail, and given distinct processes for the preparation of tetra-<sup>4</sup>,

1. In U.S.P. 779421, Holmes says after the starch has been nitrated—as described in the subsequent note, "I stabilize the nitrated starch in the following manner: After boiling in water with the addition of some stabilizing or acid neutralizing reagent which is practically insoluble in water, such as an alkaline carbonate, preferably that of calcium, I find that all traces of acid are completely removed. The carbonates of the alkaline earths produce a result impossible with the soluble carbonates as sodium carbonate, because the latter decomposes quite rapidly the nitrostarch when the solution is hot, while calcium carbonate, being a less energetic alkali, is still as efficient an antacid. The stabilizing result is marked after boiling about twenty-five hours, and after some five hours' boiling there results a compound which is exceedingly stable, as stable, in fact, as gun-cotton purified in the usual manner. After boiling has been completed the product is dried at a low temperature. In a series of subsequent patents (U.S.P. 875913, 875928, 1908) Holmes recommends the introduction as stabilizing agents in the proportion of 2-5% on the weight of the dried nitrated starch, the following substances: ammonium orthophosphate, ammonium arsenate, normal ammonium chromate, ammonium palmitate, normal ammonium tartrate, normal ammonium pyrotartrate, triammonium citrate, oxamide, thiourea, nitraniline, aniline oxalate, acetanilide, nitrotoluidine, toluidine oxalate, acetoluide, and benzamide. U.S.P. 895639, 1908, adds ammonium carbonate.

2. G. E. Arnold, A. C. Scott, and H. E. U. Roberts, E.P. 3449, 3450, 1906.

3. Ding. Poly. J., 1889, 273, 137; 1892, 284, 137. See bibliography to 1892 in Arms and Explosives, Dec., 1892.

4. Tetranitrostarch may be prepared in large quantities as follows: Potato starch is dried at 100° until constant in weight. It is then ground to a fine powder, and dissolved in nitric acid of sp.gr. 1.50. The mixture is continually agitated and cooled so the temperature remains below 25°. The charge of starch is intro-

penta-,<sup>1</sup> and hexa-nitrostarch<sup>2</sup> and recommends the moistening of 6 parts nitrojute with 2 parts starch nitrate with ethyl acetate, working the mass to a homogeneous paste and finally drying at 50°. The product so prepared contains 11.54% N, and is stated to be highly stable. The action of dilute nitric acid on starch has recently<sup>3</sup> been exhaustively investigated<sup>4 5</sup>.

**Nitropentaerythrite.** The method of Thiemé<sup>6</sup> for the preparation of this compound is to produce the pentaerythrite from the condensation of acetaldehyde and formaldehyde in the presence of lime. After fusing to 190–250°, the melt is reduced to a very fine powder dissolved in nitric acid and precipitated by sulphuric acid, the nitropentaerythrite being formed. It was intended principally as an explosive, either dry or gelatinized.

duced through an opening in the cover of the digesting vessel, there being ten times as much acid by weight as starch taken. When the starch is apparently all in solution in the nitric acid, a large vessel is filled with spent nitrosulphuric acid from nitroglycerin manufacture, the temperature of which is under control by refrigeration apparatus, and in this spent acid the nitrostarch in solution in nitric acid is slowly sprayed in by means of large atomizers, using an injector worked by compressed air. This precipitates the nitrostarch in the form of a finely grained powder. Five parts by weight of spent acid is required to completely precipitate 100 parts by weight of the nitric acid starch solution. After precipitation the nitrated starch is collected on a nitrated filter cloth, repeatedly washed until neutral to litmus, ground into an "emulsion" and treated with aniline, toluidine or xylidine, preferably the former, so that when pressed into cakes it contains about 33% water and not over 1% aniline. With the above-outlined process, Mulhäuser prepared nitro derivatives containing 10.96–11.09% N, snow white in color, becoming electrified when rubbed, very stable, and readily soluble in cold nitroglycerin.

1. Pentanitrostarch is produced along with some tetra- when 20 gm. rice starch, previously dried at 100° until water-free, is treated with 100 gm. nitric acid, sp.gr. 1.501, 300 gm. sulphuric acid, sp.gr. 1.82, and after standing for one hour the entire mass is discharged into a large quantity of water, and well washed. The washing is completed by means of a dilute solution of sodium hydroxide. The yield is about 147–149%. To separate the tetra- from the penta-nitrostarch, the mass is heated with ether-alcohol, the ether distilled off, causing the penta- to precipitate out, leaving the tetra- dissolved in the alcohol. As obtained by this method the tetra- contained 10.45% and the penta- 12.76–12.98% N.

2. Hexanitrostarch is the product chiefly formed when 40 gm. anhydrous starch is treated with 400 gm. nitric acid, sp.gr. 1.501, and allowed to remain at room temperature for twenty-four hours. The entire mixture is then run into 1,200 cc. sulphuric acid 66° Bé., and the white, flocculent precipitate formed, well washed and dried at the atmospheric temperature. The product consists of about 75% hexa- and about 25% penta-nitrostarch.

3. By A. Doroschewski and A. Rakowski, Jour. Russ. Chem. Phys. Soc., 1907, 39, 427; Chem. Centr., 1907, 2, 1325.

4. M. Berthelot gives the heat of formation of nitrostarch as 812 cal. for 1 gm. and the heat of total combustion as 706.5 cal. for 207 gm. Berthelot and Veille have determined the average velocities for nitrostarch powder.

5. A patent (E.P. 6460, 1888) has been granted to A. E. Nobel for the use of nitrostarch. He incorporates nitrostarch, nitrodextrin and nitrocellulose together with acetone and produces a homogeneous mixture, the acetone being afterwards removed by distillation.

6. U.S.P. 541899, 1895; E.P. 20281, 1894; abst. J.S.C.I., 1895, 14, 66. For nitromannite see L. Vignon and Gérin, C.R., 1901, 133, 515; Bull. Soc. Chim., 1902, 27, 24.



**Nitrates of the Carbohydrates.** W. Will and P. Lenze<sup>1</sup> have investigated the nitric esters of the bioses, trioses, pentoses, and hexoses, all well-characterized carbohydrates, the methods of nitration being designed to introduce the maximum amount of nitrogen. Starch, wood gum and other celluloses were also experimented with. As regards temperatures of decomposition, they were found to be much more stable than the cellulose nitrates. In endeavoring to determine the probable instability of the cellulose nitrates, the following summary as condensed by Cross and Bevan<sup>2</sup> represents the more important results.<sup>3</sup>

*"Monoses.* The *aldoses* are fully esterified, in the pentoses 4OH, in the hexoses 5OH groups reacting. The pentose nitrates are comparatively stable at 50°; the hexose nitrates on the other hand are extremely unstable, showing a loss of weight of 30–40% when kept twenty-four hours at this temperature.

*"Xylose* is differentiated by tending to pass into an anhydride form ( $C_5H_{10}O_5-H_2O$ ) under this esterification. When treated in fact with the mixed acids, instead of by the process usually adopted by the authors of solution in nitric acid and subsequent addition of the sulphuric acid, it is converted into the dinitrate  $C_5H_6O_2 \cdot (NO_3)_2$ .

*"Ketoses (C<sub>6</sub>).* These are sharply differentiated from the corresponding aldoses by giving *trinitrates*  $C_6H_7O_2(NO_3)_3$  instead of *pentanitrates*, the remaining OH groups probably undergoing internal condensation. The products are, moreover, *extremely stable*. It is also noteworthy that levulose gave this same product, the trinitrate of the anhydride (levulosan) by both methods of nitration.

*"The Disaccharides or Bioses* all give the octonitrates. The degree of instability is variable. Cane-sugar gives a very unstable nitrate. The lactose nitrate is more stable. Thus at 50° it loses only 0.7% in weight in eight days; at 75° it loses 1% in twenty-four hours, but with a rapid increase to 23% in fifty-four hours. The maltose octonitrate melts (with decomposition) at a relatively high temperature, 163–164°. At 50–75° it behaves much like the lactose nitrate.

*"Trisaccharide.* Raffinose yielded the product  $C_{18}H_{21}O_5 \cdot (NO_3)_{11}$ .

*"Starch* yields the hexanitrate ( $C_{12}$ ) by both methods of nitration. The product has a high melting and decomposing point, viz., 184°, and when thoroughly purified is quite stable. It is noted that a yield of 157% of this nitrate was obtained, and under identical conditions cellulose yielded 170%.

1. Ber., 1898, 31, 68.

2. "Researches on Cellulose," 1895–1900, Longmans, Green & Co., p. 42.

3. See also Cross, Bevan and Jenks, Ber., 1901, 34, 2496.

"Wood gum, from beech wood, gave a tetranitrate ( $C_{10}$  formula) insoluble in all the usual solvents for this group of esters.

"The authors point out in conclusion that the conditions of instability and decomposition of the nitrates of the monosaccharose series are exactly those noted with the cellulose nitrates as directly prepared and freed from residues of the nitrating acids. They also lay stress upon the superior stability of the nitrates of the anhydrides, especially of the ketoses."

The process of J. M. Bonneville<sup>1</sup> of acting upon sugar with nitric acid to produce a nitro derivative soluble in acetone and methylated spirit, and of especial value in lacquer manufacture, has never established its industrial value.<sup>2</sup>

**Other Nitrated Celluloses.** Various forms of cellulose have from time to time been proposed for the preparation of the corresponding nitrates, and while possessing desirable properties, have more often been brought forward in an endeavor to produce less expensive or more stable esters. In general they have not found the wide commercial applications which their advocates had hoped for, due in the main to difficulty in purification or obtaining sufficient amounts of the raw material for continued use. As far back as 1859 a waterproofing composition was devised, using nitrated white pine sawdust.<sup>3</sup> Henry Spill in 1870 attempted to use esparto grass, but had difficulty in removing the silica.<sup>4</sup> Ramie,<sup>5</sup> flax and esculapius weed<sup>6</sup> have been nitrated and worked up into plastics as dental plates. Dean prepared "nitrodextrin"<sup>7</sup> by treating bleached cotton rags with a mixture of sulphuric and hydrochloric acids, and after the rags became tender they were nitrated in the usual manner until a thick ropy mucilage was formed. The mixture was well washed with a large volume of water, the nitrodextrin allowed to collect by subsidence, and further washed until neutral. R. Bernstein<sup>8</sup> used the solid fruits, nuts and shells of trees of the palm species, particularly the fruit of *Phytelphas macrocarpa*, usually known as vegetable ivory, and of several species of "*Mauritia*," which after boiling in alkaline solutions and washed in water were nitrated in the usual manner. Dolliak<sup>9</sup> found that

1. E.P. 814, 1881.

2. A. Elliott in his article on nitrosaccharose (J.A.C.S., 1882, 4, 147) mentions amyl alcohol as a solvent of this substance.

3. J. Mackintosh and G. Rhodes, E.P. 734, 1859.

4. E.P. 1017, 1870; for an efficient method see Hengst, E.P. 18002, 1898.

5. L. Dietz and B. P. Wayne, U.S.P. 133969, 1872.

6. Bickford, Spooner and Pyroxylin Manufacturing Co., E.P. 1170, 1873.

7. G. S. Dean, E.P. 2226, 1881.

8. E.P. 12778, 1885.

9. J.S.C.I., 1885, 4, 366. For résumé of literature on nitrojute, see Cross and Bevan, J.C.S., 1880, 37, 666; 1882, 41, 90; 1889, 55, 199; C.N., 1898, 77, 300; Mulhäuser, Chem. Zeit., 1892, 16, 163; Ding. Polyt. J., 1892, 283, 88.

when rye straw is boiled fifteen hours in 1-2% caustic soda solution, and then nitrated and washed until neutral, the matted, brownish-yellow mass formed contained 11.07% N, and when gradually heated flashed at 177°. It was found to be soluble in ether-alcohol, acetone, amyl acetate and acetic acid, but decomposed at ordinary temperatures after several days, even in the presence of urea and other mild alkalis. By pulping the straw after nitration<sup>1</sup> and exhaustive washing, C. F. Hengst was able to materially prolong the stability. The Marsden Company,<sup>2</sup> advocate the use of vegetable pith, such as that of maize or cornstalk, which is first separated from the wood and fiber, boiled with a dilute alkali to dissolve the vegetable fats, sappy and other adherent constituents, the separation being assisted by repeated heating, beating and winnowing, preferably with heated air. The pith thus prepared gave a nitrate of very great solubility and low viscosity. Gorse, and similar materials have been extensively used in France<sup>3</sup> for the manufacture of nitrated cellulose intended for those plastics where complete solubility is not essential.<sup>4 5</sup>

1. E.P. 13656, 1888; see E.P. 20978, 1890, for nitration of cottonseed hulls, etc.

2. E.P. 6656, 1899; for process of nitration of horny materials, see Notelle and Leroux, F.P. 347702, 1904; for cellulose nitrates from the cellulose of the Agave plant, see A. Carneiro, Z. Schiess- und Sprengstoffw., 1909, 4, 103. For mixed esters of cellulose and nitric acid see Cross, Bevan and Jenks, C.N., 1901, 84, 61.

3. G. P. Horteloup, F.P. 347353, 1904; for manufacture from sisal, see Hollins and Taylor, E.P. 23192, 1903.

4. F.P. 327136, 1902; 331176, 1903.

5. According to L. Vignon and P. Sisley (Bull. Soc. Chim., 1891, (3), 6, 898; J.C.S., 1892, 62, 1111) when silk is immersed in ordinary nitric acid (sp.gr. 1.133) at 45° for one minute, and is subsequently washed in water, it is colored intensely yellow, and the color is unaffected by exposure to air and light, while it is deepened by the action of dilute alkali solutions. Nitric acid free from nitrous compounds does not cause this coloration, which is found to vary in intensity directly with the amount of nitrous compounds present, and with the temperature and specific gravity of the acid used. The deepening of color by alkaline solutions is independent of their causticity, while the silk increases in weight and takes up a certain amount of the base.

Silk treated with a mixture of hydrochloric acid and sodium nitrate is colored pale yellow; the color is rapidly browned on exposure to air and light, or by the action of boiling water or alcohol, while cold alkaline solutions turn it reddish brown. Silk which has been subjected to the action of nitrous acid, or of nitric oxide, in an atmosphere of carbonic anhydride, and subsequently well washed, is colorless, but is colored a stable yellow by nitric acid. Nitric peroxide colors silk yellow at once. Silk heated with nitrous acid, and then oxidized with potassium permanganate and hydrochloric acid, is colored exactly as by nitric acid (impure), from which it seems that the yellow coloration is dependent on the action of nitrous compounds, and not on the oxidizing agent.

The yellow coloration is produced by acidified stannous and chromous chloride solutions. Analyses of the nitrated silk show that about 2% of nitrogen is fixed in the reaction, probably, primarily, as the nitroso group, which the further action of the nitric acid converts into the nitro group, a carboxyl group being displaced. The properties of the product somewhat resemble Mulder's xanthoproteic acid, but this contains more carbon and less nitrogen, and results from a more intense action. Sulphuric acid dissolves ordinary silk gradually to a slightly colored solution, whereas nitrated silk is converted into a pale yellow viscid mass. Aqueous

At various times have been exploited the use of wood fiber,<sup>1</sup> esparto,<sup>2</sup> wood pulp,<sup>3</sup> hemp,<sup>4</sup> gorse,<sup>5</sup> the fiber of *Ulex Europens*,<sup>6</sup> and the flower stems of various species of Agave,<sup>7</sup> but the products have never attained commercial prominence.

Due to the persistence of J. R. France<sup>8</sup> a process for the manufacture of a cellulose nitrate for the celluloid industry was tried on a manufacturing scale in the United States in 1890. The cotton fiber was first carded and combed so as to arrange the fibers longitudinally instead of irregularly, after which they were cut off in such short lengths as to have the appearance of dust. The theory of France, and the essence of his process, was that up to that time variation in uniformity and stability of resulting nitrate was due in a large measure to obstructions in the cotton fiber, and that by comminuting the fiber, nitration would take place more rapidly and at a less cost. It is a fact that the nitrates produced by the France process were readily soluble, but it was soon determined that the yield was quite inferior, due to the passage of large amounts of cotton into solution in the nitrating fluid, while still more was lost in the subsequent processes of washing. The main difference in the ease or difficulty of nitration of various textile fibers lies in their morphological structure. When flax fiber and cotton are nitrated under similar conditions as regards time of immersion and acid strength of bath, it is found that whereas the cotton readily yields a fluid solution to amyl acetate, flax gives a difficultly soluble and glutinous mixture, due to the greater resistance to acid penetration of the cell wall. If the temperature of nitration for flax be raised higher than that for cotton, fluids of the same viscosity are obtained.

**Nitrates of Hydro- and Oxy-cellulose.** These bodies, which have never been prepared in a pure state, are of interest chiefly upon potash dissolves ordinary silk in the cold, and nitrated silk on heating; neither solution is precipitated by dilution with water, and both evolve ammonia when heated. Both varieties of silk are dissolved by hydrochloric acid and by zinc chloride solution.

Ammoniacal vapors are evolved on distillation of each variety, and a carbonaceous residue is left. For nitration of horn, see P.P. 347702, 1904.

1. W. Ruckteschell, E.P. 4349, 1885.
2. Proc. Chem. Soc., 1894, 89, 137.
3. E.P. 336, 1891; see also Engel, E.P. 6022, 1887.
4. C. F. Hengst, E.P. 13656, 1888.
5. A. Bouret and A. B. Verbiere, E.P. 24768, 1898.
6. G. Horteloup, F.P. 331176, 1903; 347533, 1904; 327136, 1902.
7. E.P. 21505, 1905; A. Carneiro, Z. ges. Schiess- und Sprengstoffw., 1909, 4, 103, finds the fibers from the flower stems to contain from 71.4-80.6% cellulose, and the ash 2.64-2.80%. The fiber was scoured with sodium carbonate, bleached and nitrated in a mixture of 1 part nitric to 2 parts sulphuric acids, the nitrogen content of the resulting product varying within the limits 11.5-12.4%.
9. U.S.P. 420445, 420447, 1890; E.P. 20973, 1890; see France, J.S.C.I., 1889, 8, 303; 1890, 9, 821.

the bearing which they apparently exert upon the stability of the cellulose nitrates. L. Vignon<sup>1</sup> has nitrated hydro- and oxy-cellulose and found that the viscosity of their ether-alcohol solutions are much lower than the normal cellulose nitrates. They are equally inflammable with the nitrates, show a greater affinity for basic dyestuffs, and are less stable. From extensive research on the higher nitrates of cellulose, hydrocellulose and oxycellulose made by Berl and Klaye<sup>2</sup> the general conclusion is drawn that the formation of either hydro- or oxy-cellulose nitrates must play a very minor part in the formation of higher cellulose nitrates at ordinary nitration temperatures.<sup>3</sup>

**Determination of Solubility.** The degree of solubility of a cellulose nitrate in a specified liquid or series of solvents should always be determined in advance, in order to judge if the pyroxylin is satisfactory for the use intended. This is especially important in the manufacture of photographic films, and in the formation of artificial filaments, for with the former, the small specks of undissolved product show up as distinct particles in the developed negative or film, and when these are magnified as in "moving pictures," they give either a continued blurred appearance or a succession of light patches fitting across the screen. With filaments, the fine specks of undissolved portions soon clog the spinning orifices and interrupt the continuity of the thread.

One method of determining the solubility is to dissolve 5 gm. of the air-dry sample in 100 cc. of the particular solvent mixture that the cellulose nitrate is to be used in commercially,<sup>4</sup> or if the viscosity is high, the solvent may be increased to 200 cc. The glass-stoppered flask is shaken frequently to facilitate solution, either alone or after the introduction of a weighed amount of shot or glass beads,<sup>5</sup> until all that will dissolve has gone into solution. Allow to stand at rest for four hours, or until the sediment has deposited, then decant carefully the supernatant liquid without disturbing the precipitate. Add 100 cc. solvent to the contents of the flask, shake vigorously and filter the precipitate through a Gooch crucible or tared

1. C.R., 1898, **126**, 1658; 1900, **131**, 509; 1903, **136**, 898, 1818; Bull. Soc. Chim., 1901, (3), **25**, 130; also J.C.S., 1895, **67**, 84; 1904, **85**, 336. For action of potash on cellulose nitrates see Vignon, Bull. Soc. Chim., 1899, (3) **21**, 597.  
2. Berl and Sprengstoffw., 1907, **2**, 381; cf., Chardonnet, E.P. 24638, 1893.

3. Cf. E. Knecht, Ber., 1904, **37**, 549; C. Piest, Z. ang. Chim., 1907, **21**, 2497.

4. The particular solvent intended to be used on the factory scale should always be taken, on account of the varying results obtained with different solvents. A pyroxylin which gives a certain percentage of undissolved residue in ether-alcohol will not necessarily give the same amount when the solvent is changed to, say, amyl acetate-benzine (60-40%).

5. In order to affect solution more quickly by disintegrating the viscous gelatinized nitrated cellulose.

filter paper, dry at 100°, and subtract the weight of the shot or beads, the difference being the weight of insoluble material in the sample taken. Usually 1–1.5 hours' drying is sufficient. Where quick and approximate determinations are to be made a portion of the 5% solution, is placed in a 10 cc. urinary tube graduated in 1/10 cc. and rotated for fifteen minutes at the highest speed. The precipitate may now be readily read off, and results obtained in this manner, in the author's hands, have proven quite satisfactory.<sup>1</sup>

**Estimation of Viscosity.** As has been stated, the viscosity of a cellulose nitrate solution is an important commercial means of deciding as to the particular use for which it is especially adapted. Uniformity in lacquers, film production and coating compositions is impossible where the viscosity and total solids of the solution are unknown. For solutions of low viscosity and containing up to 5 ounces to the gallon, a simple form of viscosimeter is sufficiently accurate, the instruments of Sayboldt and Redwood being hardly necessary. The principle, however, of allowing a given volume of fluid to pass through an orifice of known diameter at a determined temperature and taking the length of time required to do so is maintained.

A 50 cc. glass stopcock burette or separatory funnel with the aperture in the stopcock made quite, small, is used for the more fluid solutions, the time required to empty from one mark or graduation to another being recorded. As the results are but comparative, no definite standard has been adopted. Viscosity determinations are usually made in attempts to duplicate given mixtures, or to bring to an arbitrary but definite standard, as regards fluidity, various nitrocotton mixtures. Acetone is taken to dissolve the nitrate, in testing for films and coating compositions, and usually a combination of amyl acetate 65 and benzine 35 parts (by volume) for lacquers. The liquid to be examined is first brought to a definite temperature,<sup>2</sup> usually 25° being taken, a small amount poured into the apparatus and the sides carefully wetted by means of a brush to remove any air bubbles which might adhere and appreciably affect the reading. The viscosimeter is then filled, time given for air bubbles (if any)

1. A method of solubility determination often used, is to dissolve out the solvent portion and evaporate to dryness the solvent containing the nitrocotton in solution. This method gives uniformly high results, due to the difficulty of removing the last traces of solvent, an entirely soluble nitrate often giving—apparently—102–104%.

2. This is quite similar to the method of Stahl (Nürnberg) described by L. E. Andes (Rev. Fett-u. Seifen, 1911, 11), in which is determined the number of seconds required for an air bubble of fixed volume to pass from bottom to top of a glass cylinder of definite height filled with the test sample at 17.5°.

to rise, and the time for a given volume of liquid to run out of the apparatus, or to fill a receptacle of known capacity placed under the instrument, determined by means of a split-second watch. There are two sources of error in this method. The evaporation of solvent while passing through the air may be sufficient so that duplicate determinations with the same sample are inadvisable, or the solution may be so viscous that a large portion may adhere to the sides of the instrument.

The principle of the Cochius viscosimeter (Fig. 2), consists in measuring the time required for a bubble of air to ascend a certain distance up the tube. The apparatus is filled by opening the stop-cock *b*, and pouring in at *a*, after removing the stopper. The size

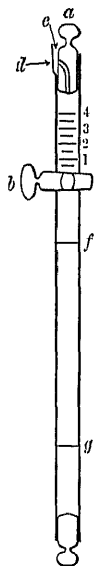


FIG. 2.—Cochius Viscosimeter.

of the air bubble is determined by the height to which the tube is filled and by the graduations, 1, 2, 3, 4, a convenient size bubble being 2 cc. Stopper *a* is inserted, cock *b* closed, and by turning the stopper, the boring *d* is brought opposite the little opening *e*, in order to relieve any internal pressure. The stopper is then tightly shut, and the apparatus inverted and fastened. The bubble is now just below the stop cock. By quickly turning the cock through 90° it is fully opened, the bubble begins to rise, and by means of a split-second watch the time required for the center of the bubble to pass from *f* to *g* is observed. The number of seconds required for the bubble to pass from one mark to the other may be called the viscosity number. The distance from *f* to *g* is arbitrary, it being evident that the longer the distance the more closely concordant will be the results. From 0.8–1 meter length between *f* and *g* and 100 cc. capacity are convenient dimensions. In the absence of such an instrument, a glass tube of about 2 meters in length may be taken, of 40–80 mm. internal diameter, one end being closed, the other

stoppered. A mark is made by scratching the glass about 25 mm. from each end. The heavy solution having been reduced to the desired temperature for the observation, is poured into the tube until the latter is nearly full. A small sphere, usually a marble or steel ball from a ball-bearing wheel, is thoroughly rubbed with the solution in order to disentangle the air bubbles that might otherwise cling to the ball, then dropped into the solution in the tube, which is then stoppered. By inverting, the time can be determined of the passage of the

ball between the marks on the tube. This apparatus, while apparently crude, is nevertheless susceptible of quite accurate work, and possesses the added advantage of allowing any number of duplicate determinations to be made by simple inversion of the tube.<sup>1 2</sup>

**Determination of Nitrogen by Lunge Nitrometer.** (See Fig. 3.) Carefully weigh out 0.6–0.7<sup>3</sup> gm. of the previously dried nitrocotton in a small weighing bottle of 10–15 cc. capacity and add from a pipette or burette 10 cc. concentrated sulphuric acid. Gently rotate the bottle until the nitrate has entirely dissolved. The fluid is then carefully transferred to the cup of the nitrometer,<sup>4</sup> the pressure tube of the instrument having first been raised so as to bring the mercury in the measuring tube up into and filling the orifice of the stopcock. Now lower the right-hand or pressure tube just sufficient to cause the solution to be drawn into the bulb of the measuring tube when the tap is slightly opened. Close and rinse the weighing bottle and stopper with 10 cc. additional sulphuric acid and transfer into the bulb in the same manner as before. Finally wash down the sides of the cup with small portions of sulphuric acid, using about 10 cc. in all, and, after allowing this to be drawn into the bulb as before, the stopcock is securely closed.<sup>5</sup> The solution being all in the measuring tube the pressure tube is again slightly raised and the tube containing the dissolved nitrate vigorously shaken for a period of ten minutes. It is then replaced in a clamp, the pressure relieved by lowering the

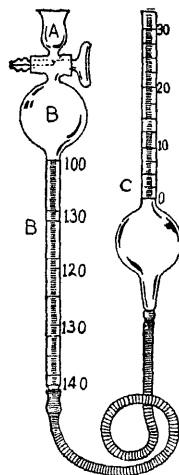


FIG. 3.—Lunge Two-bulb Nitrometer.

(A, cup; B, measuring tube; C, pressure tube.)

1. The accuracy of the temperature of the solution is an important factor. Lunge records an instance where a pyroxylin solution gave a viscosity of 20.35 seconds at 14°, while with a rise in temperature to 25.25°, but 14.18 seconds were required. From this it is seen that viscosity rapidly decreases with increase of temperature.

2. An alternate method is to use, instead of a ball, a float nearly the size of the tube, and used in a manner similar to an Erdmann float in a burette. The speed of motion of the float can be regulated by its diameter, i.e., the more nearly the diameter is to that of the tube, the more slowly will the float ascend.

3. Depending on the nitrogen content of the nitrocotton. An amount must be taken so that the volume of NO shall be greater than 100 cc. but less than 150 cc. The nitrometer capacity should be 150–200 cc., and contain a bulb at the top of 100 cc. capacity. The stopcock—which is three-way—must be very accurately ground.

4. Or where the nitrate has not been finely pulped it may be weighed directly into the nitrometer cup, the acid added, and after stirring with a glass rod until dissolved, transferred into the measuring tube and rinsed with sulphuric acid in the usual manner.

5. Great care is necessary to prevent the admission of air bubbles and the pressure tube must be only slightly lowered or the vacuum formed will cause the acid mixture to run in with a rush—difficult to control—and carry air along with it.



When any gas-volumetric operation has been carried out in *A*, the volume of gas is not read in the ordinary manner after adjusting the mercury in *A* and *C* to equal levels. Before taking the reading of the volume of gas in *A*, the three tubes are so adjusted that the mercury in *B* stands at the 100 cc. graduation, and the levels in *A* and *B* are the same.<sup>1</sup> This adjustment is most readily carried out in the following manner: The tube *A* is securely clamped while *B* and *C* are raised, *C* to such an extent that the mercury in *B* rises to the graduation 100 cc. *B* and *C* are then lowered simultaneously, so that the difference of level of the mercury in the two tubes is maintained until the mercury stands at equal levels in *A* and *B*, in the latter still at the 100 cc. graduation.<sup>2</sup> It is obvious from the above, that by the use of the gas-volumeter all thermometric and barometric readings, and all reductions by calculation or special tables, are avoided; the volume of gas is read off directly under conditions corresponding to the normal pressure and temperature. As it is not easy to shake the mercury and sulphuric acid in the tube itself when a reduction tube is attached, and as there is danger of the gas going over into the reduction tube, it is advisable to induce the decomposition in a separate apparatus, *E* and *F*, Fig. 4, and then transfer to the volumeter for measurement. *E* is the reaction vessel of capacity of about 100 cc. when used for the analysis of nitrous vitriol, and of about 200 cc. when used for the analysis of dynamite and nitrocellulose. It is provided with a tap, a beaker *c*, and pressure tube *F*, arranged as in the ordinary nitrometer.<sup>3</sup> To carry out a determination, *F* is first raised until the mercury reaches the end of the capillary *a*, which is then closed with a ground glass or rubber cap *b*, to prevent the escape of mercury on shaking, and the tap of *E* also closed. The material to

occupy at the observed temperature and pressure, either dry or moist, is then calculated by means of the above formula. For method of measuring dry gases with a wet reduction tube and conversely, see Lunge, "Technical Methods of Chemical Analysis," 1908, v. 1, pt. 1, p. 141.

1. The gas volumes in *A* and *B* then correspond to such temperature and pressure that their volumes are equal to those which they would occupy when dry at 0° and 760 mm. pressure, since this condition (if properly conducted) is insured once for all in the case of *B*, and the gas in *A* is at the same temperature and under the same pressure.

2. The adjustment will be found a trifle inexact, which can be remedied by a correction of *B*. In cases where another liquid is introduced into the measuring tube besides mercury, the pressure which it exerts must be taken into account. For instance, in nitrogen determinations by the Dumas method, a mark is made below the 100 cc. graduation of the reduction tube, corresponding to one-tenth the height of the potassium hydroxide solution in the measuring tube, the sp.gr. of which may be taken as 1.10 that of the mercury. In then reading off the volume of nitrogen, the mercury in the reduction tube is brought to the 100 cc. graduation, and that in the leveling tube to the special mark below, by which means the height of the potassium hydroxide solution is allowed for.

3. *E* is best supported by a ring, and *F* by a clamp.

be determined is introduced in the usual manner through the cup *c*, the reaction induced by shaking, and the whole allowed to stand to regain atmospheric temperature. *E* and *A* are then brought to the same height, as shown in the figure, and the mercury in the measuring tube of the volumeter *A* driven over to the end of the thick rubber tube attached to the capillary *d*. The cap *b* is then removed, the capillary *a* slipped into the rubber connecting tube until glass touches glass, *F* raised and *C* lowered, the two connecting taps opened, and the gas syphoned from *E* to *A*. The tap on *A* is closed as soon as the acid from *E* reaches the bottom of the capillary tube *c*. The levels in *A* and *B* are then adjusted, and the mercury in *B* brought to the 100 cc. graduation, as described above.<sup>1</sup> By the use of several reaction vessels, many more determinations can be carried out in a given time than is possible with the ordinary nitrometer.

**Determination of Nitrogen Oxides.** The lower nitrogen oxides are estimated by allowing a weighed or measured volume of the acid to flow from a burette graduated in 1/20 or 1/50 cc., into a measured volume of half normal potassium permanganate solution (never the reverse) diluted with 4-5 volumes of distilled water previously warmed to 40°. The quantity of permanganate required varies directly with the amount of nitrous acids present. 1 cc. N/2  $\text{KMnO}_4 = 0.009502$  gm.  $\text{N}_2\text{O}_3$ .<sup>3-4</sup>

**Determination of Mixed and Spent Acids.** Three reliable methods of determining the composition of the mixed acids are as follows:

(a) Total acidity is determined by titration of a 2 cc. sample

1. This method of transferring gas is advantageous, not only because the pressure due to the sulphuric acid does not have to be allowed for, but also because the unavoidable dirtying of the apparatus is confined to the reaction vessel *E*, which is readily cleaned. Care should be taken that the bores of the capillaries *a* and *d* are not enlarged at the ends, so that no bubbles of gas will adhere upon connecting up.

2. At ordinary temperatures the reaction proceeds too slowly, while if the temperature be too high or the solution too concentrated, hydrated manganese dioxide separates out and gives trouble, but does not prevent titration from being carried out, since the oxide again goes into solution after the titration is completed.

3. If the volume of permanganate solution taken be denoted by *x*, and the volume of nitrous vitriol required to decolorize by *y*, the weight of nitrous oxide ( $\text{N}_2\text{O}_3$ ) in gm. per l. is expressed by the formula  $\frac{9.502x}{y}$ . To express the result in  $\text{HNO}_3$  or  $\text{NaNO}_3$  instead, the factors 15.75 or 21.258 are substituted above for the 9.502.

4. Undue prominence has been given to the action of the nitrogen oxides in nitrocotton manufacture. Often in the purchase of mixed acid from manufacturers, the amount of nitric oxides (calculated as  $\text{N}_2\text{O}_3$ ) is limited to 0.05%. After rebuilding the spent acid a number of times the low oxides will increase to 0.2-0.3%—a negligible quantity. For nearly all purposes, this amount of oxides can be calculated as its equivalent in nitric acid by ignoring them entirely. No difference in the nitrocotton can be found if this method be followed where the oxides are not in excess of 0.3-0.4%. (See J. R. Pitman, J.S.C.I., 1900, 19, 645.)

the weight of which has previously been determined by a 100 cc. pycnometer, using  $N/2$  NaOH. Sulphuric acid is obtained by the usual gravimetric precipitation with a barium salt. Nitrous acid is estimated by diluting a portion of the acid mixture, neutralizing with sodium carbonate or hydroxide and treating with potassium ferrocyanide and citric acid.<sup>1</sup> The total acidity less the sum of the nitrous and sulphuric acids represents the nitric acid present.

(b) Determine the specific gravity by pycnometer or hydrometer and the oxides of nitrogen by the permanganate method. The total acidity is then obtained as described above, and calculate it as  $HNO_3$ . Determine the nitric acid by the nitrometer and subtract the percentage found from the total acidity, the difference being sulphuric acid.<sup>2</sup>

(c) The method of Mihr<sup>3</sup> eliminates the use of the nitrometer. He claims to determine mixed acids both fresh and spent with an accuracy of 0.1% by titration first of the total acids as described above and then of the sulphuric acid which remains after volatilization of the nitric acid by evaporation on the water-bath. If nitrosylsulphuric acid is present, it must first be decomposed by the addition of water before evaporation.<sup>4</sup>

**Unaltered Cellulose** may be estimated by boiling a small sample with sodium stannite<sup>5</sup> solution, carefully washing out the stannite with warm water and drying. The cellulose nitrates are dissolved by this treatment, leaving the unchanged cellulose as the residue. Or a weighed sample of the ester is shaken with ether-alcohol until no more dissolves filtered and the filtrate shaken with ethyl acetate and acetone until no more passes into solution. The ether-alcohol dissolves the lower nitrates and the ethyl acetate and acetone the higher nitrates, the undissolved residue being unchanged cellulose.

1. G. Coffetti and G. Maderna, *Gaz. chim. ital.*, 1907, (2), **37**, 13; *J.S.C.I.*, 1907, **26**, 1008.

2. The calculation of results would be as follows: Total acidity, say, 96.2%. Nitrogen by nitrometer, 16.8%; difference 79.4%. Then  $\frac{79.4 \times 49}{63} = 61.76\%$

$H_2SO_4$ , 49 being one-half the mol. wt. of  $H_2SO_4$  and 63 the mol. wt. of  $HNO_3$ .

3. Fr. Mihr, *Chem. Ztg.*, 1907, **31**, 324, 340; cf. A. P. Van Gelder, *J.S.C.I.*, 1900, **19**, 508.

4. Although Lunge (*Z. ang. Chem.*, 1904, **18**, 1681) finds this method gives values for nitric acid too high on account of a loss of sulphuric acid on evaporation, it has the advantage over the nitrometer for nitric acid in spent acids, for any cellulose nitrate in solution gives up its nitrogen in the nitrometer and is calculated as so much nitric acid. The author has worked with this method, and where the evaporation is conducted at low temperatures and water added once or twice during evaporation, very concordant results are obtained comparative with the nitrometer for unused mixed acids.

5. It is best to prepare the sodium stannite solution just before use, the time as required, and this may be done by adding a solution of stannous chloride to stannous chloride, until the precipitate first formed just dissolves.

The unconverted cotton may also be determined by boiling a fresh quantity of the air-dry sample (usually 5 gm.) with a saturated aqueous solution of sodium sulphide. After allowing to stand at a temperature of 40–60° for two or three hours the mass is decanted or filtered, and the process repeated in the same way. The insoluble residue, which consists of unnitrated cellulose is first washed with dilute HCl, then water, dried and weighed. In more accurate work the cellulose is finally ignited and the weight of the ash deducted.<sup>1</sup>

**Preparation of Acid-Proof Nitrated Filter Cloth.** According to Claessen<sup>2</sup> in order to prepare filter cloths so as to render them acid resisting, the cloth is first immersed in cold nitric acid of 40–50° Bé., then in concentrated sulphuric acid of about 60° Bé., finally washing with water until neutral. By this method a superficial nitration only is effected. According to the author, a filter cloth which will stand strong acids can only be prepared by weaving it from artificial threads made from pure nitrocellulose solution. F. Bayer & Co.,<sup>3</sup> state that completely nitrated cloth with 12.4–12.9% nitrogen, may be produced by immersion first in nitric and then in sulphuric acids,

1. The method of Lunge (J.A.C.S., 1901, **23**, 538) is satisfactory in more highly nitrated products, but is not applicable to the lower nitrates, which Lunge attributes to the fact that as these esters are prepared with less concentrated acid, they invariably contain oxycellulose. The reagent employed is an alcoholic solution of sodium ethylate,  $C_2H_5ONa$ , although sodium methylate or amylate would have the same effect and is made by dissolving 2 or 3 gm. metallic sodium in 100 cc. 95% ethyl alcohol, the solution being filtered and mixed with 100 cc. acetone. This reagent has no effect on unaltered cellulose, even after several hours' contact, while the cellulose nitrates are almost instantly decomposed with formation of a reddish-brown substance soluble in water (evidently the sodium salt of an organic acid, perhaps oxypyruvic acid, Will, Ber., 1891, **21**, 400). The operation is carried out as follows:

150 cc. of the 200 cc. prepared above is placed in a capsule or Erlenmeyer flask along with 5 gm. of guncotton. The mixture is heated to 40° or 50° on a water bath, and now and then shaken up during twenty or thirty minutes; or else it is allowed to stand at the ordinary temperature for a few hours. It is then allowed to settle. The brown-red solution is decanted from the undissolved portion; the latter is first washed with alcohol by decantation, and subsequently with water, whereby the brown substance is dissolved. The residue, consisting of cellulose, is filtered and washed with hot water, last of all with addition of a little hydrochloric acid. For ordinary work, it may be at once dried and weighed; for very exact estimations the water is removed by washing with alcohol, the residue is once more treated with 50 cc. of the reagent left over from the first treatment by keeping at 40° or 50° for fifteen minutes, and the operation is finished as above. The cellulose thus obtained does not yield a trace of gas in the nitrometer and gives only an extremely faint blue reaction with diphenylamine. It shows a very faint yellow color, produced by about 0.1 mgm. of the brown substance which can be removed by treating with a solution of 0.1 mgm. chloride of lime in 5 cc. very dilute hydrochloric acid; but this last treatment is really unnecessary, as the 0.1 mgm. does not appreciably affect the estimation. The results agree to 0.1 or 0.2%, if the weight of unchanged cellulose amounts to about 0.2 gm., which can be attained by employing a convenient weight of the cellulose nitrate.

2. Zeit. ang. Chem., 1906, **20**, 317; C.A., 1907, **1**, 1169.

3. Zeit. ang. Chem., 1906, **20**, 571; see also J. Wetter, E.P. 17302, 1897; F. Sparre, U.S.P. 850266, 1908.

and that the cloth so prepared is superior in quality and strength to that formed from weaving threads, being nearly twice as strong, and more resistant to acids and chlorine, while more open and porous than the latter. The author has often nitrated a whole undergarment (shirt or union suit) which was completely soluble in amyl acetate and contained 11.5-12% N.<sup>1</sup>

Cramer<sup>2</sup> recommends employing filter papers consisting wholly or partially of nitrocellulose, in order that incineration may be more rapid and complete. Such papers also offer the additional advantage of filtering very rapidly and of not being quite as hygroscopic as ordinary filter paper. In this respect they approach in properties the toughened or hardened filter papers. Where the filter is highly nitrated and burns too freely, a small amount of paraffin may be added to lower the speed of ignition.

1. To produce solid cloths for protective purposes against acids, D. Bachrach (U.S.P. 692102, 1902) recommends the addition of graphite or bitumen. About 10% of either is said to produce a cloth which will successfully resist long contact with corrosive chemicals. If it is desired to blend the nitrocellulose with the graphite or bitumen an acid-resisting solvent known as "picamer" (F. Greening, E.P. 22019, 1894) may be used to dissolve the nitrated cellulose. Picamer may be obtained by fractionating wood-tar distillate with chromic acid or alkaline potassium bichromate. See also the process of E. Müller, E.P. 12867, 1898.

2. Zeit. ang. Chem., 1894, 8, 269; see also Hargreaves, E.P. 24235, 1894.

## CHAPTER III

### THE NITRATION OF CELLULOSE

**Historical.** After Schönbein had announced his discovery of the ballistic possibilities of the cellulose nitrates, he immediately applied for patent protection for his discoveries, and the first United States patent for a cellulose nitrate was granted to him Dec. 5, 1846.<sup>1</sup> Apparently it attracted little attention in this country, on account of inability to control the manufacturing processes and the poor quality and stability of the ester produced. Eighteen years afterward, when Lenk introduced his process<sup>2</sup> and gave a specific series of steps for preparation,<sup>3</sup> interest in the manufacture became more general.<sup>4</sup> It was not until 1866, however, when Abel obtained protection for his pulping process,<sup>5</sup> and showed conclusively that the stability is greatly increased by breaking the cotton fibers in order to eliminate all acid from the inner filamentous canal, that the manufacture of the cellulose nitrates may be said to have assumed definite commercial importance.<sup>6</sup> Following up Abel's idea of the importance

1. U.S.P. 4874, 1846; E.P. 11407, 1846, taken out for him by his friend, John Taylor.

2. U.S.P. 43166, 1864; cf. F. Greening, U.S.P. 172995, 1875; E.P. 4806, 1876.

3. Among others, the impregnation of the nitrocotton with a solution of water glass.

4. Revy, U.S.P. 50083, 1865, used cotton spun into a lightly twisted yarn, and purified by previously washing in an alkaline solution. Like Lenk, water glass was used as the final acid neutralizant.

5. U.S.P. 59888, 1866.

6. This process with its refinements was widely used from the time of its patent protection until comparatively recent times. Nathan (J.S.C.I. 1909, 28, 180) describes the process as formerly carried out at Waltham Abbey, England, as follows:

"The nitrating acid was composed of 3 parts of sulphuric acid of 96% monohydrate to 1 part of nitric acid of 91% monohydrate, thoroughly mixed and cooled. This acid was run from the store tanks into cast-iron dipping pans, holding about 220 lb. each, the pans being supported in an iron tank through which cold water circulated, to keep the temperature below 70° F. The dipping pans were provided at the back with gratings, on which to press out some of the acid from the charge. The charge of cotton waste weighed 1 lb. 4 oz., and on removal from the cooling box was passed from the back through an earthenware pipe in the partition running along the back of the pans, and raked by a dipper, as rapidly as possible, into the acid. After remaining in the acid bath for about eight minutes, the cotton was removed to the grating and a portion of the acid squeezed out by means of an iron lever having an iron plate attached to one end. After a charge

of acid elimination, Schaffner devised a method of washing under pressure to compel the fluids to more thoroughly permeate the fiber.<sup>1</sup> Still difficulty was experienced in removing the last traces of acid, and crushing to an impalpable powder,<sup>2</sup> neutralizing with ammonia fumes,<sup>3</sup> and the addition of chalk were among the expedients tried. Cotton was accepted as commercially the best material to convert into nitrate, and attention was turned to the varieties and mechanical treatment of the cotton before and during nitration. Cotton dust,<sup>4</sup> cotton carded, spun, and woven into hanks were experimented with, but while the former could not be sufficiently purified, the latter forms yielded a large increase in weight in nitration, but the purification processes were unduly long, due to the physical structure of the woven and matted fibers. Maxim made a series of improvements in mechanical appliances for nitration,<sup>5</sup> Chardonnet outlined the successive

had been removed from the dipping pan about 13½ lb. of the mixed acid was run into it to replace the amount removed with the charge. The charge, now weighing with the adhering acid about 15 lb., was placed in an earthenware pot provided with a cover and transferred to the cooling pits, through which a stream of cold water flowed, and where it remained for twelve hours. During this period of digestion the conversion of the cotton into guncotton was completed. The contents of the pots were now emptied into a centrifugal wringing machine, and the bulk of the waste acid extracted. The guncotton was then removed from the centrifugal machine and placed in galvanized iron pans with long handles. These pans, when filled, were carried quickly across to the immersing tank and the guncotton thrown into a large bulk of water, the workmen standing by the tank and pushing the guncotton at once under the water with a strong wooden paddle. The immersing had to be done as quickly as possible, as, if the guncotton were allowed to come gradually in contact with water, it was liable to fume off. The immersing tank was fitted with a perforated copper plate, to allow the water to overflow, so that fresh water was constantly passing over the tank. The guncotton was kept well stirred by means of a wooden paddle. A 2 cwt. had been immersed, the inflow of water was stopped and the tank drained down. When all the water had been run off, the tank was filled up again with fresh water. This was repeated six times, or until the guncotton no longer tasted acid. When this stage had been reached the guncotton was wrung in a centrifugal machine, water from a hosepipe being turned on the guncotton for one minute during the wringing, and it was then ready for boiling.

"This process, although it undoubtedly produced a good guncotton, had certain disadvantages, and the amount of labor required was very great. The plant, although individual items were not expensive, very rapidly deteriorated, and the cost of renewals and replacements was heavy. Power was required to drive the centrifugal machines, large quantities of water were used both for cooling and immersing, and decompositions, both in the pans, pots, and acid centrifugals, were by no means an infrequent occurrence."

1. U.S.P. 60571, 1866; 93757, 1869; cf. Muschamp, U.S.P. 128450, 1872.

2. Mackie, U.S.P. 141654, 1873.

3. Anthony, U.S.P. 143865, 1873.

4. J. France, U.S.P. 420445, 420446, 1890; F. Greening, E.P. 8442, 1886.

5. H. S. Maxim, U.S.P. 430215, 1890; 454281, 465280, 1891; 474788, 479988, 1892; 544924, 1895; E.P. 4129, 1891. He impregnated the cotton with a saturated aqueous solution of sodium or potassium nitrate, dried, and then plunged this into a mixture of nitric and sulphuric acid, depending on the decomposition of the nitrate inside the cotton filament and the nitration of the same by the nascent nitric acid formed. He was the first to apply the "steeping" process in the United States, whereby the cotton was first immersed in a strong nitrating mixture and

steps in his process of pyroxylin manufacture and including centrifugal extraction.<sup>1</sup> Mowbray<sup>2</sup> and the Hyatts<sup>3</sup> made important improvements in connection with the nitration of paper for pyroxylin plastics, and the rapid advances made in photographic films composed of the collodions, all materially contributed to place the manufacture of the nitrates on a stable and definite basis.<sup>4</sup> The rise of the pyroxylin lacquer industry, the production of artificial leather and waterproof coatings, advances in pyroxylin plastics and celluloid, the attempts to produce artificial filaments in imitation of silk, and the coating of leather with dissolved pyroxylin, all contributed to the advance in manufacture and refinements in purification, by creating a large demand. This demand has steadily grown, both in volume and in exactness of purity, stability and solubility of the various cellulose nitrates produced. This demand in a large measure came as the result of successful search for suitable solvents for these esters, the development of the fusel oil industry as the means for the manufacture of amyl acetate—technically the most important and widely used liquid solvent for the cellulose nitrates—being most important and far reaching.

#### **Classes of Cellulose Nitrates Produced in the United States.**

These may be reduced, for all practical purposes, to three different series of nitrating operations,<sup>5</sup> as follows: (1) Nitration by hand of a high grade of cotton for use in fine lacquers, artificial filaments and after not over five minutes' immersion, taken out and without draining, transferred to a tank containing weak acid of many times more weight than the cotton, in which the latter was allowed to remain for several hours to "adjust" the nitration.

1. The novelty in this process (U.S.P. 455245, 1891) was in neutralizing all wash waters with an alkali and evaporating the same to dryness to recover the nitric and sulphuric acid used in nitration. Chardonnet's process was intended to produce a cellulose nitrate of great fluidity and solubility, especially applicable for the formation of artificial filaments.

2. See under Celluloid.

3. See Celluloid.

4. The earliest manufacture of smokeless powder in the United States was carried on by Charles Lennig, at Philadelphia, about 1850. He made a gun-cotton for small-arm charges out of long staple, fibrous cotton, but on account of accidents, the manufacture was soon discontinued. The next factory started was erected about 1870 by Carl Dittmar at Quincy, Mass., where a soft granulated powder was made, but this was soon abandoned. The first factory erected solely for the manufacture of modern smokeless powder was in 1890, at the U.S. Torpedo Station at Newport, R. I., being planned, erected and operated by Charles E. Munroe, under the direction of the government. It has continued and is to-day in regular operation. Following this, four factories were erected in 1891, one each in 1895 and 1898, and two in 1900. From this time the manufacture became rapid and more widely scattered.

5. A special grade of pyroxylin for the manufacture of collodion is, according to Sadtler (*Handbook of Comm'l Industrial Chem.*, 296) put upon the market by the Schering factory of Berlin, and is made by immersing cotton for fifteen minutes in a mixture of equal volumes of sulphuric of sp.gr. 1.815 and nitric acids 1.40, at a temperature of 80°.



photographic film production. (2) Nitration of paper for the highest grade of pyroxylin lacquers, for coating silverware, the manufacture of continuous films and the preparation of transparent celluloid sheets. (3) Nitration of cotton for opaque preparations as celluloid collars and cuffs, artificial pyroxylin leathers and bronzing fluids, of a low nitric acid nitrating mixture, producing an irregular and not always soluble pyroxylin, but one in which the manufacturing cost is low, and the yield comparatively high. Actual factory processes of the preparation of these three classes of cellulose nitrates are described in detail subsequently.<sup>1</sup>

#### U. S. Ordnance Requirements for Nitrocellulose Manufacture.

The following general instructions are prescribed by the U. S. Army Ordnance Department, as revised Apr. 18, 1908:

*Nitrating.* Cellulose of standard quality shall be dried at a temperature not exceeding 110°. When cold, this cotton shall be nitrated in mixed nitric and sulphuric acids. After nitrating, the nitrocellulose shall be washed in water before boiling.

*Preliminary Boiling.* The nitrocellulose shall be boiled at least forty hours, and with not less than four changes of water, in tubs so constructed that the nitrocellulose shall not come in contact with steam at a temperature greater than 100°. There shall be complete ebullition or boiling over the entire surface of the tubs. No alkali shall be used in this preliminary purification.

*Pulping.* The nitrocellulose shall then be pulped in fresh water to which may be added just enough sodium carbonate solution to preserve a slight alkaline reaction to phenolphthalein solution, the process to continue until the material is thoroughly and evenly pulped to a satisfactory degree of fineness, and shows a clean break when a handful is squeezed and broken into parts. During this process the water shall be changed to such extent as may be necessary to remove impurities.

*Poaching.* After pulping, the nitrocellulose pulp shall be run to the poachers, settled, and water decanted. The nitrocellulose shall

1. A process for the preparation of "soluble cellulose" has been described by P. Marino (E.P. 7430, 1908) in which ordinary pyroxylin is introduced into a mixture of alcoholic solutions containing about 10% (of the weight of the pyroxylin) of each of the following substances: manganese chloride, ferric sulphate, and sodium ethyl sulphate. The solution is diluted with ether or other solvent of pyroxylin and the pyroxylin is dissolved. A saturated solution of freshly precipitated ammonium magnesium phosphate is separately prepared in a quantity of hydrochloric, phosphoric, or other mineral acid equivalent to about 10% of that of the solvent used with the pyroxylin. The two solutions are mixed and heated at 25° for twelve hours. The "soluble cellulose," which separates on cooling, is drained, washed and dried. The mother liquors are collected separately, and after dilution with spirit and neutralization of the mineral acid, they may be utilized for rendering wood or fabrics non-inflammable.

then be boiled six hours in fresh water, and during this time a total of not more than 10 gal. of carbonate of soda solution for each 2,000 lb. dry nitrocellulose may be added at intervals. This solution shall contain 1 lb. carbonate of soda per gallon. During this and all other boiling in the poachers the pulp shall be thoroughly agitated by mechanical stirrers. After boiling the nitrocellulose shall be allowed to settle and the clear water decanted as completely as possible. The tubs shall then be filled with fresh water, boiled two hours, settled, decanted, and refilled with fresh water. The boiling shall be then continued for one hour, and this process repeated three times, making a total boiling treatment in the poacher as follows:

Six hours' boiling with or without sodium carbonate, settle, change water.

Two hours' boiling, no soda; settle, change water.

One hour boiling, no soda; settle, change water. Repeat this one hour boiling, three more times.

Twelve hours' boiling, five changes water, total.

After boiling, the nitrocellulose shall have ten cold-water washes, each washing to consist of agitation by mechanical means, for one-half hour in a sufficient amount of fresh water, thorough settling and decanting clear water; at least 40% of the total contents of the poacher shall be drawn off. A sample shall then be taken for subjection to the various tests prescribed for nitrocellulose. Should the nitrocellulose fail to meet the required heat test, it must be boiled again with two changes of water, the time of actual boiling being five hours, without the use of alkali, and then it must be given ten cold water washes in the manner described for the regular treatment.

**Treatment of Cotton Preliminary to Nitration.** A large number of processes have been devised to facilitate the nitrating process by a preliminary treatment of the cotton before immersion in the nitrating fluid. These processes, either intentionally or otherwise, produce various hydro- and oxy-celluloses, which are more readily attacked by nitric acid than is normal cellulose. Furthermore, it has been found possible by preliminary treatment to so modify the cellulose, that the nitrated product therefrom is almost completely soluble in 95% ethyl alcohol, and hence economy in solvent is effected. Wirth<sup>1</sup> was the first to call attention to this preliminary treatment by his patented process in which the cellulose is first obtained in a pulverulent state (hydrocellulose) either by soaking for some time in sulphuric

1. E.P. 2519, 1878. See "Impurities Found in Cotton Badly Separated from Seed," C. Beadle and H. P. Stevens, *Paper Making*, 29, 102. They found the palisade cells, composed of hemicellulose extremely resistant to bleach.

acid of a specified density, or by heating to 100° with water containing 5% sulphuric acid. It was claimed that the conversion of the dry pulverulent cellulose into pyroxylin could then be carried out by the use of less acid. Chardonnet<sup>1</sup> simply heated to 150–170° cotton in the dry state, the application of the high temperature being intended to increase the solubility of the subsequently formed pyroxylin. His process had the advantage that the cotton must have been thoroughly dried and hence in an unusually receptive state for penetration by the nitrating fluid. In the Cross method,<sup>2</sup> instead of nitrating the fiber directly, cotton is subjected to the fumes of dry HCl gas for some hours in a closed chamber, the acid carefully removed by washing, and the powder when dried immersed in nitric acid only, whereby a gummy nitrated substance is formed, which may be purified by precipitating with water and washing. Zinc chloride<sup>3</sup> or caustic alkali, carbon disulphide and water have been advocated, the latter combination being the well-known viscose. A convenient method of preparing these amorphous degradation products of cellulose is to immerse cotton in a mixture of 5 parts by weight of 85.5% sulphuric acid with 3.5–4% concentrated nitric acid to which 2–2.5% water has been added. The cellulose is mechanically kneaded with the acid mixture, the temperature being kept below 3°. After an hour's time, 100–120 parts nitric acid of 48° Bé. are added, when the nitration is complete in about fifteen minutes.<sup>4</sup> The introduction of carbon dioxide gas with cellulose, by heating both to a temperature of 150°, is said to so modify the cellulose structure as to render subsequent nitration much less tedious and uniform. While previous disintegration of the cellulose fiber by treatment with sulphuric acid, zinc chloride or other powerful dehydrating agents, no doubt mechanically renders nitration much easier, the great point of advantage lies in the facility with which the acid may be subsequently removed. However, it has been proven beyond a reasonable doubt that the nitrated hydro- and oxy-celluloses and sulphuric esters decrease very materially the stability of the cellulose nitrate, and mainly for this reason, treatment previous to nitration is at present not extensively practiced.<sup>5</sup>

1. E.P. 19560, 1891.

2. Cross, Bevan and Beadle, E.P. 9284, 1892.

3. A. Luck and A. Durnford, E.P. 4769, 1895; cf. E.P. 116, 1904.

4. Patronenfabr. Saxonia, D.R.P. 198284, 1903.

5. See O. Schmidt E.P. 4769, 1895; 116, 1904; according to E. Nowicki (E.P. 402197, 1909) flax, hemp and ramie, or their wastes, are used as raw materials for nitration in the manufacture of pyroxylin, the fibers being bleached and purified and submitted to a mechanical preparation to bring them into a suitable state for the process. It is stated that since these fibers are devoid of cuticle, and when mechanically prepared, their central canals are open at both ends, they are far more amenable to the uniform action of the acid than cotton fibers. Moreover,

**Teasing.** As obtained from the factory, cotton waste contains colored threads which must be removed by hand, and often a considerable amount of foreign matter—wood, iron, rubber and strings—as well as knots and hard lumps. These are removed by a carding machine, where, by means of a series of iron-teeth rollers the fiber is pulled out and separated, and the lumps opened up. The apparatus of J. France<sup>1</sup> is useful for this purpose.

Where short- or long-fiber cotton is used as the source of cellulose rather than cotton waste, two methods of separating and picking are used in the United States, depending on the length of the

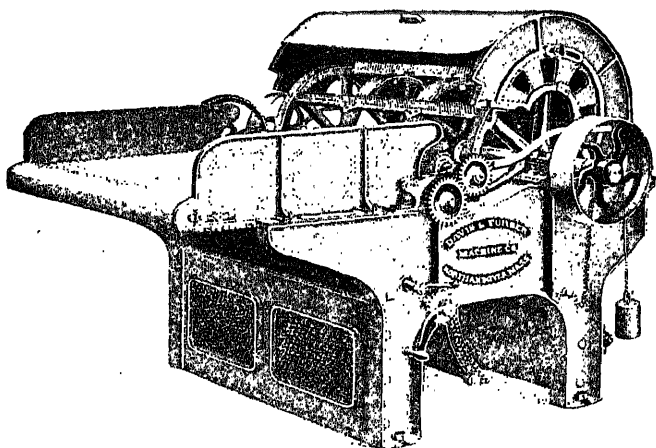


FIG. 5. --The Davis & Furber Mixing Picker for Cotton.

cotton fiber. For that length corresponding to "linters" and longer, the Davis & Furber "Mixing Picker" with pin-feed roll and shell (see Fig. 5) is the type of machine giving most satisfactory results.<sup>2</sup> In recent years, however, the application of cotton has been greatly extended by the gradual use of fibers of shorter length, and for picking such cottons the "Coggswell Mill" (see Fig. 6) has been the type

the finished product may be compressed to a greater density than nitrated cotton. If desired, these fibers may be mixed with cotton or other cellulose fibers before nitration.

1. E.P. 20964, 1880; 5361, 1890.

2. The machine is heavily constructed, consisting of a main cylinder fitted with special teeth, together with a feed apron and roll. The cotton is received by the feed apron, carried to the feed roll, the latter holding the stock while the revolving teeth in the cylinder tear it apart. The cylinder revolving at high speed carries the disintegrated cotton around and throws it out at the back of the machine, or into a suction pipe, where it is carried over into the dry house. These machines, which are of large capacity, open up the cotton in such a manner as to make it fluffy and feathery in appearance.

widely used, it consisting of two-ribbed disks revolving at high speed in opposite directions.<sup>1</sup> By means of connection with a Sturtevant or other suction blower and pipe connection to the dry house, which is usually located near the picking house, the cotton after passing through the picking machine is automatically carried over to the dry house, where by means of shut-offs located in the carrying pipes in the several drying chambers, the cotton may be blown into any dry-room desired.

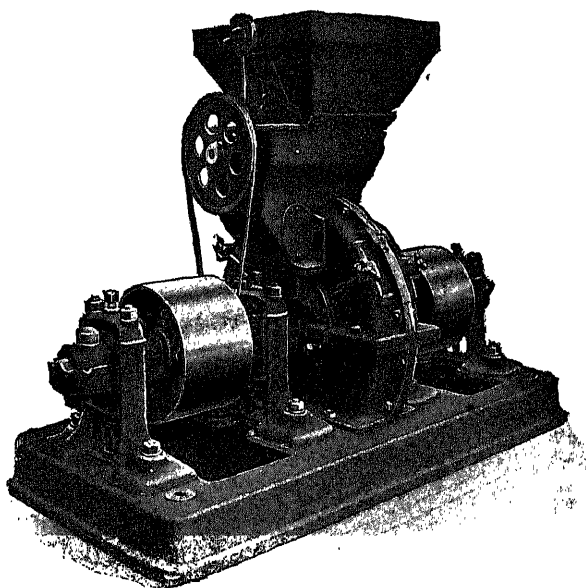


Fig. 6.—The Cogswell Mill for Picking Cotton.

**Scouring.** Before the cellulose can be considered in fit condition for nitration, it must be rendered "absorbent"<sup>2</sup> by removal of

1. Manufactured by the A. & F. Brown Co., New York city. The mill is run with two belts, one cross and one straight, which drive the grinding disks in opposite directions at a speed of about 2,000 revolutions per minute. All that is needed for the successful operation of the mill is a well built, well balanced counter-shaft for high speed, with a friction-clutch pulley for starting the mill up slowly, and a heavy, immovable foundation, so there will be little or no vibration. When properly set up, the mill requires no skilled labor to operate. The only adjustment needed is the turning of the tail pin one way or the other as the material may be wanted, coarser or finer. After the mill has been running a few months it is good practice to reverse the belts, thus giving a fresh wear to the grinding surfaces. The plates are about the only parts which require renewing, and under favorable conditions may last upward of two years.

2. On the surface of the individual fiber there is a protecting layer of wax and oily matter, while in the central canal is the dried remains of the protoplasmic material. The object of the boiling out and scouring processes, is, of course, the removal of these materials. When purified from adhering fatty and waxy materials

the natural occurring vegetable fats and waxes, and this is best done by boiling under pressure in zinc-lined wooden vats or kiers with dilute aqueous sodium carbonate (soda ash)<sup>1</sup> for several hours, and until a sample taken out, washed, dried and extracted with ether yields not more than 1% ether extract.<sup>2</sup> Whereas raw natural cotton will float on the surface of water—often for hours without becoming completely wetted—a properly scoured cellulose when thrown into water should sink within two minutes.

**Bleaching.** After the alkali from the scouring process has been entirely eliminated by washing, the coloring matter in the fiber is removed by bleaching,<sup>3</sup> usually with calcium hypochlorite<sup>4</sup> (bleaching powder). The method of G. J. Atkins<sup>5</sup> consists in the treatment of cotton with potassium chloride and "oxychloride,"<sup>6</sup> the claim being made that the silica is also removed.<sup>7</sup> The process of bleaching cellulose after nitration<sup>8</sup> has never passed beyond the stage of patent protection.<sup>9</sup> E. Berl and Klaye<sup>10</sup> and Berl and W. Smith,<sup>11</sup> have studied the influence of the previous treatment of cellulose, especially bleaching, upon the properties of the resulting nitrates in the laboratory, and C. Piest<sup>12</sup>

the cotton becomes very absorbent, which quality is explained on the supposition that the ripe cotton fiber is made up of a series of tissues of cellulose, separated by intercellular material, in this way forming a series of capillary surfaces capable of inducing considerable capillary contraction upon any liquid in which the fiber may be immersed.

1. The author's experience is that sodium hydroxide (caustic soda) should never be used, on account of its energetic action on cellulose. (See Viscose.) Crystallized sodium carbonate (10H<sub>2</sub>O) is often employed on account of its supposedly milder action. See J. Parson, *Textile Mfr.*, **31**, 387.

2. According to A. Hertzog (*Centralbl. f. Textile Ind.*, 1890, **21**, 975) the German military authorities require a cotton which when treated with ether yields not over 0.9% fat; when nitrated does not disintegrate; and containing only traces of chlorine, lime, magnesia, iron and sulphuric and phosphoric acids. See also "Inspection of Cotton Waste for Manufacture of Gun-cotton," C. E. Munroe, *J.A.C.S.*, 1895, **17**, 783.

3. C. Piest (*Z. ang. Chem.*, 1908, **21**, 2497), found that bleaching appears to have a greater effect on the formation of reducing substances than does treatment with alkali, has determined by the reducing action of Fehling's solution on cotton (Schwalbe, *Chem. Abst.*, 1907, **1**, 1696, 2179), the oxycelluloses giving lower nitration products than cellulose under similar conditions.

4. Where bleaching powder has been used, it is exceedingly difficult to wash out all traces of chlorine, a minute trace of which may cause the nitrated cotton to turn slightly acid after drying.

5. E.P. 7058, 1903.

6. Prepared according to E.P. 5596, 1901.

7. Removal of silica by digestion with hydrofluoric acid is never resorted to commercially.

8. G. M. Mowbray, U.S.P. 349658, 1886, the pyroxylin being decolorized by a hydrochloric acid acidified solution of oxalic acid.

9. For structure of cotton fiber as affected by bleaching see Geo. Witz, *Bull. Soc. Ind.*, Rouen, 1883, **10**, 416; Nastjukow, *Bull. Mulh.*, 1892, 493; R. Haller, *Z. Farb. Ind.*, 1907, **6**, 125.

10. *J.S.C.I.*, 1907, **26**, 1157.

11. *Z. ges. Schiess- u. Sprengstoffw.*, 1909, 81.

12. *Z. ang. Chem.*, 1909, **22**, 1215.

has repeated and corroborated their work commercially. Cotton was subjected to the following treatments: (1) Bleaching for forty-eight hours in bleaching powder solution of 3–5° Bé; (2) and (3), bleaching for eight days in solutions prepared by mixing 2–5 k. and 5 k. respectively of bleaching powder with 5 l. of water; (4), mercerization by treatment with 18.5% caustic soda lye for twenty minutes; (5), heating for ten hours at 150° in a current of carbon dioxide.<sup>1</sup> The results obtained showed that with a given nitrating acid and temperature of nitration the nitrocellulose prepared from strongly bleached cotton has a somewhat lower nitrogen content and a considerably higher solubility in ether-alcohol than that prepared from ordinary cotton. The solubility of the nitro-compound in absolute alcohol increases as the cotton is more strongly bleached. Nitrocellulose from strongly bleached cotton is more difficult to stabilize than that from ordinary cotton. The stabilized nitrocellulose is more soluble in ether-alcohol than the non-stabilized product. Nitrocellulose from mercerized cotton has a slightly lower nitrogen content, a much higher solubility in ether-alcohol, about the same solubility in absolute alcohol, and is more difficult to stabilize than that from ordinary cotton. Nitrocellulose prepared from cotton which has been heated in a current of carbon dioxide has a slightly higher nitrogen content, about the same solubility in absolute alcohol and in ether-alcohol, and is more difficult to stabilize than that from ordinary cotton. O. Guttman,<sup>2</sup> has made experiments during a period of two years with samples of cotton, from English and German sources, the history of which was known, from their obtainment from the cotton-spinning works to the finished, and in some cases, stored nitrocellulose. Some of the samples of cotton were unbleached, others had been strongly bleached with bleaching powder; and some were highly contaminated with dust, etc. The results obtained confirm those of Piest, namely, that the stronger the degree of bleaching of the cotton, that is, the higher the content of oxycellulose, the more difficult it is to stabilize the nitrocellulose obtained therefrom, and the more soluble is the nitro-derivative in ether-alcohol, and in addition the solution has a lower viscosity.

**Drying.**<sup>3</sup> One method is to place the cotton in a large steam-jacketed iron cylinder, steam being made to circulate in the surround-

1. D.R.P. 199885, 1908; abst. J.S.C.I., 1908, 27, 937.

2. Z. ang. Chem., 1900, 22, 1717.

3. The object of the removal of moisture is to prevent dilution of the nitrating fluid. Damp cotton nitrates much faster, is more difficult to control, fumes more readily, the yield is decreased due to solution in the nitrating acid, the spent acid is further diluted by the water in the cotton, and the finished product forms a more fluid solution.

ing jacket, the temperature of the inner chamber being from 70–90°. Circulation of air is maintained by means of a compressed-air reservoir, and enters the cylinder from the bottom. From the 7–10% moisture present in the raw cotton at the end of five or six hours, this should be reduced to not over 0.6%.<sup>1</sup> Or the cotton may be placed in large rooms on wire screens heated from below by series of steam pipes, a slow current of dried air being passed under the shelves and through the cotton. As soon as the drying process has been completed the heat is preferably either continued until the cotton is to be used or the charges are weighed out into milk cans or other suitable receptacles, covers clamped air-tight and allowed to cool.<sup>2</sup>

**Acids used in Nitration.** The nitric<sup>3</sup> and sulphuric acids universally employed are commercial products of a high degree of purity. The sulphuric acid must be reasonably free from lead, and the nitric acid contain no hydrochloric acid. It is also important that they should contain no solid impurities which might adhere to the nitro-cotton, and which would interfere with the subsequent recovery of the waste acid or lower the stability. In recent years it has been possible to obtain at a reasonable cost Nordhausen fuming sulphuric acid, often called "oleum," and its use has enabled a larger proportion of spent acid to be revived economically than was possible when the strongest commercial sulphuric acid was of 63° or 66° Bé. strength. Whereas formerly it was the custom to purchase acids of a certain strength, and mix them in the desired proportion, discarding the spent acid, now the system is being adopted of mixing large quantities in steel or cast-iron tanks ("acid eggs")<sup>4</sup> analyzing the mix-

1. A weighed sample should then be taken from the top of the cylinder and the moisture determined by drying in a water bath at 98–100°, for one hour and re-weighing. For description of suitable apparatus see Sanford, "Nitro-explosives," 59.

2. During the cooling, which requires from four to six hours—depending on the size of the charge—the cotton often re-absorbs about 0.5% moisture, thus making about 1% in the cotton just before nitration.

3. For action of nitric acid on cellulose see H. de Mosenthal, *J.S.C.I.*, 1904, 23, 292.

4. Saposchnikoff (*J. Russ. Phys. Chem. Soc.*, 1901, 36, 669; *Z. physik. Chem.*, 1905, 51, 609) has studied the behavior of mixtures of sulphuric and nitric acids. He finds that addition of water to mixtures containing less than about 60% of sulphuric acid causes a diminution in the vapor pressure, the effect being less as the percentage of sulphuric acid is increased. With mixtures containing more than 60% of sulphuric acid, however, addition of water causes an increase of vapor pressure. This is due to the fact that with high percentages of sulphuric acid some of the nitric acid is dehydrated to nitric anhydride, which, on the addition of water, is again converted into nitric acid. Also that a satisfactory acid mixture for nitration purposes must fulfill two requirements. It must contain sufficient nitric acid to give the desired reaction-velocity and degree of nitration; and its properties must be not appreciably altered by the water separated during the nitration. Mixtures which best answer the first condition, have, however, the disadvantage that the volume-concentration of the nitric acid is strongly diminished



ture, and adjusting the composition by the addition of nitric or sulphuric acids, to obtain the desired percentage composition. The nitrating acid consists of the maximum of waste acid, which can be used and still be built up to the desired percentages of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . In the preparation of the lower forms of the cellulose nitrates the water is always increased in the nitrating mixture above that required for guncotton.

The nitrating acids are usually stored and transported in iron drums or tank cars. It has been found that the concentration of the sulphuric acid must not be much below a sp.gr. of 1.60, or the iron is attacked, hydrogen evolved and the acid decomposed. Mowbray's claim<sup>1</sup> for the use of Bessemer steel tanks as being superior on account of insolubility in sulphuric and nitric acid has not received general acceptance. Iron is brought into the passive state by concentrated nitric acid, which, therefore, has but very little dissolving effect on it.

**Direct Dipping Process.** The following description of this process is that of Sir F. Nathan.<sup>2</sup> The installation consists of parallel double rows of long iron tanks known as "coolers." Iron pots termed "dippers" in which nitration is carried out stand in the coolers, 62 to each cooler. Sliding wooden covers rest on the coolers to guide the fumes from the dippers into earthenware pipes with openings at intervals, through which they are drawn by exhaust fans. The mixed acid, either cooled or warmed as necessary, is carried by lead pipes placed between each row of coolers, and is supplied to the dippers through earthenware cocks at intervals.

**Nitration.** The water in the coolers is kept at  $15^\circ$ . The dippers, having been placed in position in the coolers, are each filled with 127 lb. of mixed acid by measurement, from the acid taps.  $4\frac{1}{2}$  lb. of cotton waste are steeped in each dipper. To minimize decompositions each charge of cotton waste is added in about ten installments. The wooden covers are only removed to allow steeping to be done, and are then at once replaced. The temperatures of nitration are: Initial temperature of mixed acid,  $15^\circ$ ; maximum after steeping,

by addition of water. A mixture must therefore be chosen which has a vapor pressure less than the maximum, but which will bear an addition of water without notable alteration. In the case of mixtures containing a relatively high percentage of sulphuric acid, an addition of water must be made in order to prevent dehydration of the nitric acid, with formation of nitric anhydride. The composition of acid mixtures for nitrating purposes may be varied within wide limits, but the author considers that for the preparation of high nitrated guncotton, the best results will, in general, be obtained with mixtures of nitric acid of sp.gr. 1.48 with from 65-75% of sulphuric acid. Probably the most suitable mixture is nitric acid, 24.29%; sulphuric acid, 65.80%; and water, 9.91%.

1. U.S.P. 350498, 1886. See Fig. 7.

2. J.S.C.I., 1909, 28, 181.

25°; temperature at end of nitration, 20°. The duration of the nitration varies according to the output required from the plant. One, two, or three shifts may be worked per twenty-four hours, and the time of nitration may therefore be twenty-four, twelve, or eight hours respectively.

The average composition of the mixed acid for a twelve hours' immersion is as follows: Sulphuric acid, 75.0%; nitric acid, 15.75%; nitrous acid, 1.30%; water, 7.95%. For an eight hours' immersion a higher percentage of nitric acid and less water is used; for a twenty-four hours' immersion less nitric and more water. The average composition of the waste acid for a twelve hours' immersion is: Sulphuric acid, 77.8%; nitric acid, 11.0%; nitrous acid, 1.5%; water, 9.7%.

*Recovering the Waste Acid.* When the nitration is complete, the "dippers," covered with light aluminum lids, are placed on barrows, wheeled to the centrifugals, situated at the end of the "coolers," and the whole contents tilted out into the centrifugal. Four dippers are loaded into each centrifugal, and the guncotton having been uniformly spread round the basket, the centrifugal is run for six minutes, to remove waste acid. At the end of that time about 1 lb. of waste acid is still adhering to each pound of guncotton. The centrifugal cover, made of light aluminum, is not fixed to the centrifugal in any way, so that as little resistance as possible may be offered when there is a decomposition. This is the usual arrangement in the case of acid centrifugals. The cone of the centrifugal projects through a circular opening in the center of the lid and is covered by a small loose aluminum box. Small holes are cut in the sides of this box, and are of service in warning the workmen when there is a decomposition, as fumes are generally seen to issue there first.

*Drowning the Guncotton.* When the waste acid has been removed the guncotton is quickly lifted out of the centrifugals and thrown under the revolving paddles of the drowning tanks, which immediately immerse it. The men who do the discharging are provided with rubber gloves and wear thick flannel hoods, which completely cover the head, arms, and breast. The hoods are fitted with strong glass windows, and are connected by light rubber tubing to a supply of pure compressed air.

*Prewashing.* After a given quantity of guncotton has been drowned, the water in the tanks is run off and the guncotton thrown onto draining tables forming part of the drowning tank. It is then loaded into the prewashing centrifugals, the acid water wrung out, and washed for a few minutes with cold water from a hose, to remove adhering acid. No special precautions, however, are taken to remove all

acid at this stage. The bulk of the water having been removed, the guncotton is loaded from the centrifugals into bogies, and conveyed to the boiling house.

The 62 dippers in each cooler form a "charge." Eight charges are worked by each shift. The yield is 159% of dry guncotton on the dry carded cotton. The output per shift consisting of seventeen men is, therefore:  $4.5 \times 159 \times 62 \times 8 \div 100 = 35.49$  lb.

**Nitration of Cotton by Hand.** One at least, of the large pyrox-  
ylin manufacturers in the United States nitrates by hand a special grade of cotton which produces a very superior pyroxylin adapted for lacquers and bronzing liquids. Whether due to intentional misrepresentation to cover "secret processes" or a deficiency of intimate knowledge of the several steps involved, a large number, if not the majority of the recipes and methods to be found in text-books and the technical literature for preparing a nitrocotton best suited to this class of work are either directly misleading in some essential step, or else the methods of manipulation described are vague and lacking in detail. Aside from the interest attached to the method about to be described from the fact that the ester so produced has for many years answered the requirements of an exacting trade as to clearness, elasticity and strength, the details represent the successive steps in a commercial process in which there have been no recent essential changes, and in which, therefore, the nitrocotton produced has stood the test of time as regards commercial acceptability.<sup>1</sup>

That grade of medium-fiber Southern cotton known as Memphis Star is used in the unbleached state, the cotton being twice scoured. The first treatment consists in steaming in a 3% (calculated on the weight of cotton) solution of sodium carbonate crystals (washing soda<sup>2</sup>) for six hours in zinc-lined wooden vats, with tightly fitting

1. Of the many methods for the preparation of pyroxylin to be found in the literature, the very great differences from each other both in composition of acid and method of procedure, make it quite a hopeless task to one of but little experience to select a method which will produce a given product. The lack of explicit information as to the condition of the cotton, temperature of nitration, duration of the operation, how to overcome the exigencies that are apt to arise during the progress of the process, yields, nitrogen content and solubility in a given solvent, render a great number of published methods incomplete, or of little value. Perhaps in no other series of industries are the factory details more carefully guarded than in the industrial preparation of cellulose nitrate compounds.

Memphis Star is an upland cotton, and its fibers are very soft, moist, and elastic, of light creamy-white color. This color is partially lost during scouring and nitration. The staple is short and the twist inferior to other grades, the straight, ribbon-like filaments being quite numerous. The cotton is carded but not bleached or scoured. It contains considerable half and three-quarters ripe fiber, which is extremely thin and transparent, distributed throughout the bulk of the pattern.

2. It has been repeatedly asserted that factory experience apparently shows that the hydrated form of sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) exerts a less drastic action on the cotton than the anhydrous form (soda ash) of sodium carbon-

zinc-lined covers. At the end of this period the cotton is washed with water until the alkali has been practically removed, when the operation is repeated. This time the steam is kept on for ten hours, and the amount of sodium carbonate reduced to 2%. The final washing is continued until the cotton is neutral, the wash water being clarified by passing through large sponge or sand filters. Scoured in this manner, dried cotton seldom gives more than 0.28% ether extract. Although in appearance cotton prepared in this manner is not as white as when bleached, the treatment results in but little change of the cellulose molecule.

The nitration is conducted in 5 gal. stoneware pots with tightly fitting lids in the top of which has been bored a  $\frac{3}{16}$  inch hole for the escape of any fumes, and which also serves to warn the workmen of the commencement of burning or "fuming" of a "batch." The cotton is dried at 105° until no further loss in weight occurs, a 2½ Av. lb. charge placed in air-tight containers similar to milk cans with rubber gaskets, and kept in a room at 35–40° until ready for use. The charge of 2.1 U.S. gal. of nitrating mixture at a temperature of 56° is run into each pot, the latter having previously been placed in a water bath consisting of a wooden vat with perforated bottom and heated by steam. The acid mixture consists of 85.1–85.2% total acids, of which 56% is sulphuric acid, leaving 29.1–29.2% nitric acid and 14.8–14.9% water. The cotton in small portions is immersed in the acid by means of aluminum forks, the handles of which are rubber covered to better prevent slipping. The heat of reaction from immersion of the cotton causes the contents of the nitrating pots to rise about 8–9° above the entering temperature of 56°. After thoroughly stirring the cotton into the acid, the false bottom of the water bath is raised until the pots are entirely out of the water, where they remain until the temperature has subsided to 56° again, which usually requires about an hour. During this first hour the cotton is stirred only enough to guard against local overheating<sup>1</sup>. At the

etc. The author has wondered if the small amounts of hydroxide sometimes found in commercial soda ash could account for the above belief.

1. Whenever red fumes are observed during the nitration process, the mass in the pots must be carefully but very thoroughly stirred. During the entire process the cotton must be stirred no more than absolutely necessary, for stirring disintegrates the fiber, and causes loss in washing. One of the main points in favor of the Turner displacement process is the fact that the cotton is not broken during nitration, and hence larger yields are obtained. If it is desired to make the cotton more fluid, the initial nitration temperature may be raised to 58° or 59°, and if this does not have the desired effect, instead of allowing the pots to cool to 56° in the air as in the original process, they may be placed in the water bath at once. It is the first temperature that governs most strongly the production of a fluid nitrocotton. From the action of the first batch in the nitration mixture subsequent batches can be modified. Three men nitrate 65 pots in one working

end of six hours' immersion the nitration is considered complete. The contents of the crocks are dumped into a centrifugal, the acid extracted and the cotton "drowned" by plunging into a large volume of cold water in the usual manner. Neutralization is effected by boiling alone, and without the addition of alkali.<sup>1</sup> The nitrocotton is pulped, and dried on cloth screens, by means of a current of filtered dry air which enters so as to pass through the nitrocotton from the bottom upward. The ceiling and walls of the dry-house are plastered, the cement floor being covered with linoleum or rubber.<sup>2</sup> The workmen wear sewed rawhide sandals. The temperature is automatically regulated between 30–35°. Usually three days are required for drying, the moisture being about 22% as the nitrocotton leaves the hydro-extractor. The nitrogen per cent is within the limits 12.65–12.75, usually nearer 12.65%.<sup>3</sup> The nitrocotton is above 98% soluble in ether-alcohol, above 96% soluble in a mixture of amyl acetate 60 (by volume) and benzine 62° Bé., 40, this latter solvent mixture being of much more importance in the lacquer industry than ether-alcohol, the latter solvent being seldom used. The viscosity<sup>4</sup> is governed in the nitrating pots largely by the following observations:

day of ten hours. In nitrating, if it is found that the physical condition of the pyroxylin will stand it, the temperature of the water bath is raised from 55° up to as high as 65°, this rise tending to increase the fluidity and clearness of the pyroxylin when dissolved, but at the same time slightly decreasing the yield. Notwithstanding theory to the contrary, it is the observation of the nitrating workmen that on damp, heavy, foggy days, the nitric acid in the nitrating fluid decomposes more readily; the nitrocotton tenders more easily in the pots and requires more careful attention to preserve the yield. The value of sulphuric acid is not, as has often been assumed, due merely to its power of combining with water formed during the reaction, but also perhaps to the formation of sulphuric acid esters, subsequently converted into nitric esters. The longer then, within reasonable limits, the cotton is left in contact with the acids, the more complete probably will be the conversion into nitric acid esters. The sulphuric esters according to this view, therefore, are merely transition bodies.

1. In corroboration of the experience of others, it has been found that when alkali is omitted, the pyroxylin requires fewer washings for neutrality, and gives longer stability tests.

2. To prevent vermin from entering the building, and the impalpable pyroxylin dust collecting in cracks.

3. At this particular works a large number of experiments have been undertaken to determine the reason why a pyroxylin solution once filtered will, or will not, deposit from 1–6% solid matter (lower cellulose nitrates) upon standing in solution in daylight. Careful comparisons of nitration formula, viscosity, original solubility and percentage of nitrogen have not resulted in conclusive results. It is not a function of temperature and is a subject of considerable moment to manufacturers of lacquers, photographic films and artificial silks. Pyroxylin intended for artificial leather and the less expensive finishing fluids is never dried, but hydroextracted either in centrifugals or by other means, and the remainder of the moisture removed by displacement with a pyroxylin non-solvent as denatured ethyl alcohol or the lower fractions of fusel oil.

4. A desired viscosity is obtained by blending pyroxylin of a viscosity higher and lower than that required. The "viscosity factor" is an arbitrary number used, and obtained by taking the grams of pyroxylin per hundred cc. in a given

(1) If the first pot nitrated tenders too much, as indicated by the "feel" with the stirring rod, the viscosity will be too low, and subsequent batches are to be put in at a slightly lower temperature, perhaps 53–54°.

(2) If the cotton falls to the bottom of the nitrating fluid, feels harsh, and but little chemical action is evident, the acid is probably deficient in nitric acid, and a higher temperature of immersion must be taken, or the nitrocotton will have a high viscosity and in the majority of cases a high insoluble residue in amyl acetate-benzene.

(3) If the cotton in the nitrating acid floats to the top (heaves), buoyed up by the nitric oxide fumes evolved, this indicates a slight excess of nitric acid. Such a batch must be watched closely and stirred at frequent intervals to prevent fuming.

(4) If the cotton in the nitrating bath feels soft ("mushy") the sulphuric acid is evidently in excess, and if the heat of reaction does not give the normal rise,<sup>1</sup> the yield will be poor, and probably contain much insoluble matter.

While the length of time is stated as six hours' immersion, climatic conditions and the humidity of the atmosphere apparently makes a difference in the nitration time, and irrespective of the length of immersion the batches are considered finished when they have a certain softness or "feel" to the workmen when the batch is stirred with a fork. Large yields are not sought, but rather fluidity and solubility in the nitrocotton is the first consideration. Something in the way of yield must be sacrificed in order to obtain high fluidity, because the higher temperatures required to obtain a desired viscosity always cause an appreciable loss of nitrated cotton, not only from passing into solution in the reacting mixture, but also in the subsequent washings, especially after having been pulped.

The dried product is tested for its suitability for certain classes of lacquers and bronzing fluids, by dissolving 1 gm. in 60 cc. amyl acetate and 40 cc. benzene.<sup>2</sup> The following observations of the solvent combination and multiplying by the time required to pass through the orifice of the viscosimeter.

1. It requires ordinarily about fifteen minutes to attain the maximum rise, and an additional thirty minutes for the temperature to return to that of the nitrating acid before cotton immersion.

2. The pyroxylin is first moistened with 30 cc. amyl acetate and after having been stirred until homogeneous, is diluted with the balance of the solvent, previously mixed. In this manner much more rapid solution is effected than by the addition of 100 cc. of the above mixture at one time; benzene, it will be remembered, is a non-solvent of any form of cellulose nitrate, being used only because it is the cheapest commercial anhydrous fluid. Cellulose nitrates may be more soluble in amyl acetate than in the above mixed solvent, but the latter is used because it approximates the formulas used in manufacture. A pyroxylin which entirely dissolves in both amyl acetate and amyl acetate-benzene 60 to 40, will have an appreciably higher viscosity in the latter solvent mixture.

tion so formed have been found generally true for the specific nitrating formula given above.<sup>1</sup>

If the solution in amyl acetate-benzine is:

(1) Thin and turbid, the total percentage of nitric and sulphuric acid was too low, that is, there was too much water present during nitration.

(2) Heavy and turbid, the temperature of the nitrating acids was too low at the time of immersion, or the cotton was not thoroughly stirred therein, probably the former.

(3) Thin and clear, yield about 140-144% (calculated on the weight of the cotton as dried at 105°); all nitrating factors right.

(4) Heavy and clear. Nitric acid high, sulphuric acid low; temperature low, nitration process fully six hours, cotton floated to top of batch during nitration period and required careful attention.

It is evident that a certain amount of skill and cleverness embraced in the word "experience" is necessary for the success of any technical process, and especially in a process of nitration which introduces several variables. But it is not too much to state that careful attention to the details as above enumerated in the hands of a person of moderate experience will enable that person to continually produce a nitrocotton especially adapted to the preparation of modern pyrox-  
ylin lacquers.

**Nitration by Centrifugals.** Nitration of cotton was originally carried on in iron dipping pans, fresh acid being added from time to time, and after squeezing out the bulk of the acid, the cotton was transferred to earthenware pots to complete the nitrating process. Later on the charge of cotton was increased by the use of larger pots or cast-iron pans holding up to 10 k. of cotton, the process being carried out with carefully prepared acid mixtures, which were fortified, as at present, by the addition of stronger acids. In 1890 Chardonnet patented the process<sup>2</sup> of placing the nitrated cotton in a centrifugal in order to obtain the maximum of spent acids, this being the first definite application of the centrifuge to the nitration of cotton. Kron<sup>3</sup> made some mechanical improvements on Chardonnet's method, but

1. These results are mean results obtained from testing each day's product for many months, and in connection with the daily reports from the nitrating house as to the deportment of the cotton in the nitrating acid. Where the nitric oxides are in excess in the nitrating mixture, a higher rise in temperature than usual occurs when the cotton is first immersed; incipient decomposition of the nitric acid is more liable to occur (i.e. the spent acid is unusually weak); the temperature falls more quickly after the maximum has been reached; the time of immersion is decreased; and more attention by the workmen is required to prevent fuming and to preserve the normal yield.

2. E.P. 5376, 1890; abstr. J.S.C.I., 1891, 10, 566.

3. E.P. 13612, 1891; abstr. J.S.C.I., 1891, 10, 1029.

it remained for Selwig and Lange in 1891<sup>1</sup> to combine the nitrating and squeezing of the spent acid in one and the same receptacle, a centrifuge. Their original apparatus consisted of a perforated revolving basket inside the nitrating shell, the cotton being converted in the machine, after which the mixed acid was allowed to run off, the remainder being removed by the centrifugal action. The nitrocotton was then immediately taken out and immersed in a large volume of running water.<sup>2</sup> L. Morane<sup>3</sup> has devised a method in which the cotton is nitrated in a slowly revolving drum, the speed of rotation being afterwards increased so that the acid is forced through a perforated casing, up helical partitions in the drum, where the acid flows over the cotton again. By this device the cotton avoids contact with the air during nitration, and so prevents the escape of fumes and the absorption of moisture by the nitrated cotton while still saturated with the acids.<sup>4</sup> This idea of "acid circulation" has been extended by Johannes Selwig,<sup>5</sup> the best known patterns being those manufactured by Selwig & Lange, of Brunswick, Germany.

The principal feature of this firm's nitrating centrifugals consists in the combination of the nitrating apparatus with the centrifugal.

The latest and most improved construction of this new centrifugal (Figs. 7 and 8) is an acid circulation device, by means of which the entire quantity of acid contained in the centrifugal, and not that contained in the drum only, works on the substance to be impregnated and participates in the nitrating process. It is worked from underneath and with a firmly fixed spindle, whose drum *d*, and also, at the same time, the iron casing surrounding it, can be filled with acid without the bearing of the spindle coming into contact with the same. The acid is led off, after the nitrating process is completed, by a special escape-cock *h*, made of stoneware, or by a valve made of steel casting.

A second and smaller escape-cock *k* permits the acid in the centrifugal to be collected separately by itself. For the purpose of the circulation of the acid, the middle hollow part of the drum, the so-called drum-cone *t*, is provided with a large number of perforations, and lengthened downward in the form of a ring. Above the bottom of the casing, and at a small distance from it, lies a second ring *r*, whose

1. E.P. 10747, 1891; abst. J.S.C.I., 1892, **11**, 635.

2. Selwig obtained patent protection (E.P. 6409, 1903) for a combination of nitrating and washing apparatus, where the nitrocotton was washed with steam after nitration, without being removed from the centrifugal. It is not used in the United States to the author's knowledge.

3. E.P. 24561, 1899.

4. See E.P. 3177, 1902, J. B. Alliot.

5. U.S.P. 764776, 1904; E.P. 6409, 1903; 7511, 26666, 1901; 23920, 1905; F.P. 312602, 1904.



outside edge reaches almost to the side of the casing, while its inner nearly touches the extension of the drum-cone already mentioned above.

There is, therefore, by this arrangement, a direct connection between the interior of the drum-cone and the outside part of the inner chamber

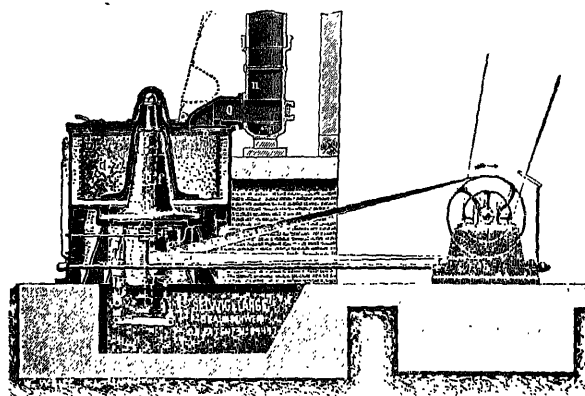


FIG. 7.—Selwig & Lange Nitrating Centrifugal, with "Acid Circulation."  
(Side view.)

of the casing. If the centrifugal is now filled to a certain height with acid, and the drum put into rotation slowly (from 24-30 revolutions per minute), then the acid participates in the motion, its surface, while sinking in the middle of the drum, rises at the edge of the casing,

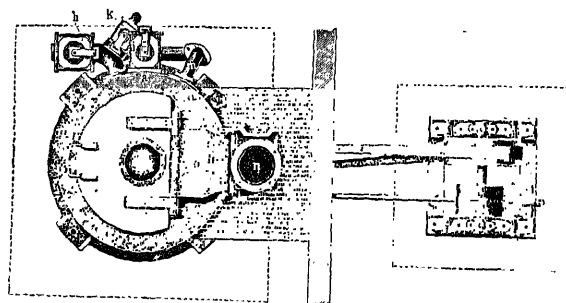


FIG. 8.—Selwig & Lange Nitrating Centrifugal, with "Acid Circulation."  
(Top view.)

where, therefore, a higher pressure of the acid exists than that in the middle of the centrifugal. This high pressure is now transmitted to the hollow chamber of the drum-cone, and causes the acid to flow through the holes of the cone into the drum, where a lower pressure

exists. The acid now flows through the substance under treatment in a radial direction, making its exit through the perforated walls of the drum into the outward chamber of the casing, from where it flows back again, under the floor  $r$ , into the interior of the drum-cone.

According to this, the acid circulates through the cotton or other substance as long as the drum continues in rotation.

The centrifugal can be made to move quickly or slowly as desired, by putting one or other of the two loose pulleys—which are arranged on the transmission shafting at both sides of the fixed pulley, and which run at different speeds—on to the fixed pulley, the quick-running pulley being then driven by the principal transmission, the slow-moving pulley by a slow-moving intermediate transmission.

In order to exhaust the nitric acid vapors during the process, and to throw off the material undergoing treatment, the centrifugal is connected with a stoneware exhauster by means of the support  $o$  and the collecting-pot for condensed acid  $n$  arranged near it. This conveys the vapors to the chimney or to a condensation appliance.

From the above details, it will be seen that by means of the acid-circulating appliance an uninterrupted intimate mixture of the acid is effected, and in such a manner that at a certain fixed moment acid of the same composition and with the same temperature can be made to penetrate throughout the material under treatment. When, therefore, proper raw material of a regular texture is used, a nitrated product is obtained which possesses great uniformity and approximately the same chemical and physical characteristics.

In the older form of nitrating centrifugals, the cast-iron bottom of the centrifugal was also the bottom of the vessel containing the acid, a construction which hindered the work and rendered frequent repairs necessary, for the cast-iron could not resist the effects of the acid for any lengthened period. The new type of centrifugal built by Selwig & Lange is provided with patent acid-holders<sup>1</sup> which are made entirely of steel plate, so that the acid cannot come in contact with cast iron at any part.

At the lowest point of the oblique bottom the escape  $q$  is fixed, the pressed conical interior of the bottom surrounds the conical upper part  $l$  of the cast-iron bearing, and the angle-iron riveted on to the bottom of the holder rests on the under frame, to which it is firmly held by means of a few clamp screws. When these are loosened and the conduction pipes screwed off, the entire holder can be easily taken down. In case, therefore, an acid-holder becomes defective, it can be easily and conveniently removed for repairs and its place supplied

1. D.R.P. 168852, 174576, 1906.

by a reserve holder. Another advantage consists in the fact that air, which enters through a few holes on the angle-ring fixed on the bottom of the holder, can be sucked through the intermediate chamber between the upper conical part *f* of the bearing and the conical inner part of the holder. The spindle bearing is thereby well cooled

and ventilated and withdrawn completely from the influence of the acid vapors.

Another improvement in nitrating centrifugals consists in the automatic cotton-steeping appliance (Fig. 9) invented by H. Wolfshohl, Spandau, near Berlin,<sup>1</sup> first patented in England in 1905, the corresponding French patent being No. 359625 of the same year.

It has been used to some extent in the United States, and apparently with satisfaction. It is claimed by the inventor that its use materially reduces the volume of nitrogen oxide fumes. (In this connection see Selwig & Lange, E.P. 11929, 1900; F.P. 243983, 1891.)

Up to the present the usual method of feeding the nitrating centrifugal consisted in one workman throwing the material in small quantities into a drum which is filled with acid, the drum rotating slowly all the time, while another workman pushed the sub-

stance under the acid by means of a fork. This method, which is somewhat inconvenient, has been considerably simplified by means of Wolfshohl's patent, and to such an extent that the second workman is usually unnecessary.

The apparatus is made entirely of aluminum,<sup>2</sup> and consists of an oblique holder *h*, fixed on the cover of the centrifugal by means of a hinged sheet-metal flap *i*, which, filling up the space between the cone

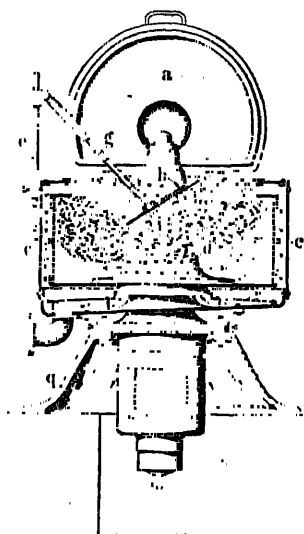


Fig. 9.—Wolfshohl Automatic Cotton Steeping Appliance for Nitration, by means of which the service of one workman may be dispensed with, the volume of Cotton Nitrated per day and its Quality being Unaffected. The manufacturers also claim that the quality of nitro-cotton produced is more uniform both in nitrogen content and solubility.

1. E.P. 23920, 1905.

2. According to Deville, Wurtz, Hunt, Langley and Roscoe (Bull. de la Soc. Ind. de Rouen, 1891, 232) aluminum is entirely unaffected by nitric and sulphuric acids, and this is borne out by the author's experience.

of the drum and the casing of the same, dips almost entirely into the acid contained in the drum. By means of a spring rod *g*, which is connected by a joint to the support *e*, the flap *i*, which pendels round the upper horizontal edge, is pressed downward, but in such a manner, however, that it can come out somewhat above when pressed from below. In the drum itself is a horizontal tappet of flat aluminum fixed between the cone and the mantle.

Before commencing to feed the centrifugal, the steeping apparatus is fixed on the cover of the centrifugal by means of a pressure screw, and the drum then made to rotate slowly (24-30 revolutions per minute), and in such a direction that its contents move against the under surface of the flap *i*. The cotton or other substance is now thrown into the acid, in front of the apparatus, but not in very large quantities. The contents of the drum are made to partake of the movement by means of the tappet, so that when the cotton is thrown in, it also rotates. As soon as it comes to the oblique holder *h* and the flap *i* it is carried right through under both by the strength of the current of the acid, and is therefore thoroughly steeped in the same. The drum is fed until it contains a sufficient quantity of material, whereupon, by loosening the rod *g* from the flap, the whole steeping-arrangement can be taken off, and placed into a stoneware pot near the centrifugal, where it remains when not in use.<sup>1</sup>

Selwig & Lange have recently patented<sup>2</sup> an arrangement for feeding paper into the nitrating vessels. The apparatus consists of a vertical stem suspended from a traveling carriage, which can be adjusted over any of the nitrating vessels. At the lower end of the stem is situated a reel of paper, the paper from which passes over a guide roll and between a pair of drawing rolls also carried by the stem. The drawing rolls are operated by means of a belt driven by an electric motor mounted at the upper end of the vertical stem. An oscillatory motion may be imparted to the stem if desired.

1. According to their circular the Selwig & Lange's nitrating centrifugals are supplied in the following sizes:

No.	External Diameter of Drum.	Height of Drum.	Capacity		Charge of Cotton.	Revolutions per Minute.	H.P. Necessary	
			of Drum.	of Casing.			Starting.	Running.
1	39.4 inch. (1,000 mm)	15 inch. (380 mm)	56 gal. (200 l.)	77-88 gal. (375-400 l.)	22-26½ lb. (10-12 k.)	about 1,000	9-10	2-2.3
2	33.5 inch. (850 mm)	14.2 inch. (360 mm)	39 gal. (175 l.)	82 gal. (ca. 255 l.)	14½-17½ lb. (6.5-8 k.)	about 1,150	7-8	1.7-2

2. F.P. 409220, 1909.

In the acid circulation centrifugals of Selwig & Lange the same acid is re-pumped over the nitrated cotton. In order to eliminate decrease in strength of the mixed acids during the process, a method has been patented<sup>1</sup> where the acids are either partially or completely renewed, continuous circulation being employed. The nitrating acid thus remains of a definite composition throughout all stages of the conversion.

**The Thomson Displacement Process** of cotton nitration, devised by J. M. Thomson and W. T. Thomson, is designed for the nitration of cotton for a wide variety of uses. In England, where the process was perfected and first patented in 1903,<sup>2</sup> so-called "gun-

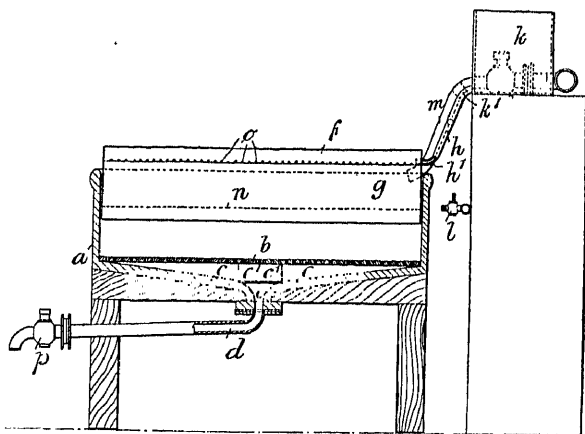


FIG. 10.—Thomson Displacement Apparatus for Cotton Nitration. (Sectional elevation.) *a*, tank; *b*, false bottom; *c'*, ribs; *d*, drainage outlet; *e*, grid; *f*, troughs; *g*, aprons; *h*, *h'*, pipe and branches to troughs; *l*, water supply pipe; *m*, pipe leading from nitrating acids; *o*, perforations in trough; *p*, cock to remove spent acid.

cotton proper"—those cellulose nitrates of highest nitration and insoluble in ether-alcohol with nitrogen content of around 13.5%, and intended for blasting gelatin and torpedo work—having been used exclusively in England at Waltham Abbey since August, 1905. In the United States this process was first tried on an experimental scale in February, 1908, actual production being commenced some three weeks later, at the Government Picatinney Arsenal, Dover, N. J., Major Odus C. Horney, commanding, where it has been in operation continuously since, this being the only place in the United States, to the author's knowledge, where this process has been carried on.<sup>3</sup>

1. H. Diamanti, P. Loisif, and H. Champin, F.P. 377425, 1906.

2. E.P. 8278, 1903; F.P. 364981, 1906; no U.S.P. granted up to Jan. 1, 1911; abst. J.S.C.I., 1904, 23, 560.

3. Through the courtesy of Major Horney, the commanding officer, the author

In the original specification of the inventors, the patent claims are based upon the discovery made by them, that the acid extraction and preliminary washing operations in cotton nitration may be combined by removing the acids from the nitrated cellulose directly by displacement without the employment of either pressure, vacuum or mechanical appliances, and at the same time securing the minimum dilution of the acids. They also observed that if water be carefully run on the surface of the acids in which the nitrocellulose is immersed and the acids slowly drawn off at the bottom of the vessel, the water displaces the acid from the interstices of the nitrocellulose with no undesirable rise in temperature, and with but little dilution of the nitrating acids. By this method the maximum acid is recovered in condition suitable for concentration and reuse, and the volume of water required for the preliminary washing materially reduced.

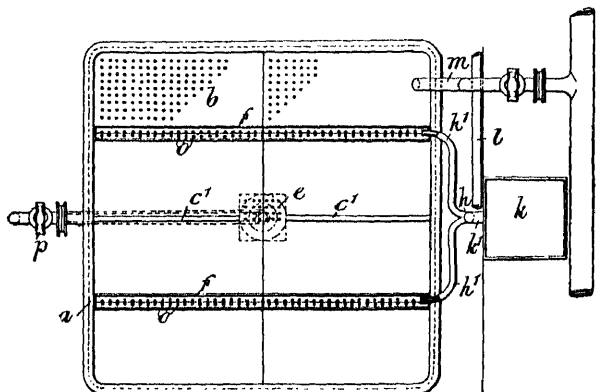


FIG. 11.—Thomson Displacement Apparatus for Cotton Nitration. *a*, tank; *b*, false bottom; *c'*, ribs; *e*, grid; *f*, troughs; *g*, aprons; *h* and *h'*, pipes to troughs; *m*, pipe to nitrating acids; *o*, perforations of troughs; *p*, cock for removal of acid.

This method has been adapted to the preparation of a pyrocollodion powder at the Picatinney Arsenal above referred to, with a nitrogen content of 12.5–12.7%, and practically complete solubility in ether-alcohol. At the present time seven units of four pans each are in daily operation,<sup>1</sup> each pan consisting of a cylindrical stoneware vessel (see Figs. 10, 11), constructed with a perforated stoneware

was permitted to see the process in operation, and from whom much of the data contained herein was obtained. The description of the English method is taken from an article by Lieut. Sir F. Nathan, J.S.C.I., 1909, 28, 181; C. N. 1909, 99, 136, 152, 159; see also "Arms and Explosives," 1906, 77.

1. Expansion in equipment in this process at Picatinney, now well under way, when completed will provide for an emergency production there of nine thousand pounds cellulose nitrate daily by this method.



FIG. 12.—The Thomson Displacement Process for Cotton Nitration, at Picatinny Arsenal, Dover, N. J.

The nitrating acid enters the pans *A*, from underneath, *B* being the one-piece perforated segmental plate placed on the bottom of each pan before the introduction of the cotton. A hood, shown faintly in the background is placed over each pan during introduction of the cotton into the nitrating acid, and by means of the flue *D*, the fumes from two pans are carried downward by suction and out of the building. A fan is located in the roof of the building which forces pure air through the apertures shown at *H*. The stream of water issues from the fourth inch rubber hose *F*, which is kept in position by means of a weight, such as a piece of lead *G*. The nitrated and washed cotton is shown at *E*. When the entire surface has been covered with a thin film of water, fuming ceases. After nitration has been completed, the spent acid is withdrawn and cold water run in so gradually that no dangerous rise in temperature takes place. A cross-section of a pan with strong and weak acid connections, hydrometer connections, etc., is shown in Major Horney's lecture on "Smokeless Powder" (our U. S. Artil., 1910, 34, (No. 105), p. 141.

false bottom which is removable, and under which is a cock at the lowest point for running off the liquid.<sup>1</sup> The nitrating acid at a temperature of 30–32°, and containing nitric acid 21–22%, sulphuric acid 63–64%, is run by gravity<sup>2</sup> into the pans, 700 lbs. in each.<sup>3</sup> The cotton—20 lb. charges for each pan—is brought into the nitrating house in sealed cans, with moisture content less than 1%, and at a temperature at least as high as the nitrating acid in which it is to be immersed.<sup>4</sup> The cotton is immersed in the acid in small portions at a time, the entire operation requiring about fifteen minutes. When the charge of cotton has been entirely immersed, the five-section perforated stoneware top plates are placed over the cotton, care being taken that all pieces of cotton are under the surface of the acid. A film of cold water<sup>5</sup> is then immediately flowed over the surface of the top plates to a depth of about one inch<sup>6</sup> in order to seal the nitrating acid and prevent fuming. The hoods which are placed over the pans during immersion of the cotton<sup>7</sup> are now removed, the cotton remaining soaking in the nitrating acid for periods varying from 1–2.5 hours, depending on the physical results desired in the nitro cotton. At the expiration of the time in which the nitration is considered completed,

1. Four pans are usually spoken of as a unit and are nitrated and emptied together. In nitrating such a unit the services of six men are required to immerse the cotton in the nitrating acid, one man to immerse the cotton for each pan, and one man for each two pans, who places the cotton onto the acid for the immersion by galvanized iron forks. A single-piece hood constructed of wood, but impregnated with paraffin oil and coated with a high congealing-point wax forms the hoods, each hood having an opening on opposite sides for the delivery of the cotton and for the submerging of it. The top of the hood, directly over the center of each pan, contains a window, over which is suspended an electric light to better light the interior of the pans during the preliminary immersion. Exhaust pipes are also provided for the withdrawal of fumes.

2. Various devices are in operation for heating the acid to the desired temperature before introduction of the cotton. In one method the acid circulates through pipes in a steam jacket or hot-water tank. Perhaps as simple and efficient as any is to encase the delivery pipe with a larger pipe containing steam connection, when by admitting steam at a given pressure, and running the nitrating acid through the inner tube at a determined volume, heating of the nitrating acid is practically automatic.

3. In J.S.C.I., 1909, 28, 181, a charge of 600 650 lb. is recommended for the production of cellulose nitrate of highest nitration, a 29 lb. charge of cotton being used.

4. From five to ten minutes is required to run in the nitrating acid per pan, depending on the force of gravity and the diameter of the entering pipe.

5. A small stream for a fourth-inch ordinary gas tubing hose is sufficient.

6. Thomson in his original patent (i.e.) suggests the use of sulphuric acid for sealing where the higher nitrated cottons are being prepared. In some cases the method may be carried out in an ordinary centrifugal, using the latter to effect preliminary drying after acid extraction. This has the advantage over the usual method of working ordinary nitrating apparatus, because the acid being removed from the cotton is gradual that practically all danger of firing and "fuming" disappears, and a greater proportion of waste acid is recovered.

7. The hoods may be transported around the nitrating room by means of a traveling crane.



the cock leading to the waste pipe is gradually opened, the waste acid allowed to flow away from the nitrated cotton at the rate of about 17 lb. per minute, the volume of fluid in the pan being maintained by running cold water in on the top plates through the distributor. This displacement of acid by cold water is continued until the major portion of the acid has run out, the water following the acid through the nitro-cotton with but little appreciable mixing, this displacement requiring about forty-five minutes.<sup>1</sup> The water in displacing the mixed acids does so so gradually that the temperature of the nitrating acid in the pans is not raised. The waste acid passes out of a 3-inch pipe by means of overflow into a larger pipe, and in this 3-inch pipe floats a hydro-meter, whereby the concentration of the acid may be observed.<sup>2</sup> The cotton after the water has been allowed to drain away is shoveled into trucks, either with aluminum forks, or preferably with wooden shovels,<sup>3</sup> and wheeled to the wash house, the pans washed out and the operation repeated.<sup>4</sup>

1. The patentees found that the rate of displacement exerts a considerable influence on the properties of the resulting nitrated celluloses, and affords a means of regulating the temperature of displacement, the rate found suitable being about two inches per hour when treating highly nitrated celluloses. It is especially essential in this process that the water used be thoroughly filtered, for if the clarification of the water has been inefficient, when the top plates in the pans are removed at the close of the nitrating process, the nitrocotton immediately under the hose which supplied the water will be found in various stages of discoloration, or perhaps a dark precipitate deposited, the cotton acting like a filter to separate the solid particles. Although these particles (if present) are supposed to be removed in filtering the block of gelatinized cellulose nitrate through the "macaroni" hydraulic press, filtration of the water used in displacement through sand or sponge filters is always desirable.

2. There is more waste acid separated and reclaimed by this process than can be utilized for fortifying purposes indefinitely, the spent acid accumulating. In order, however, to obtain the desired amount of spent acid of maximum concentration, various methods have been tried to divide the waste acid into definite fractions. The specific gravity of the strongest acid as it leaves the pans and at the temperature (about 32°) is about 1.7. By now separating as the first fraction a volume of spent acid required to make up the next day's run of acid, using the strongest commercial acids obtainable, and for a second fraction, all that portion not required for strengthening, but yet sufficiently strong so as not to attack too strongly the transportation containers, seems to be the most economical solution of the problem of spent-acid recovery and utilization. It has been found that a spent acid of sp.gr. much under 1.4 attacks iron so readily as to be inadvisable for reshipment, and it is usually run into the sewer. The charge of nitrating acid for a pyrocellulion nitrocellulose usually consists of three portions: (1) The spent acid from previous nitration. (2) Sulphuric acid 98% absolute  $H_2SO_4$  (which in winter has about 1% of nitric acid added to it to prevent freezing by the formation of monohydrate crystals) and (3) a mixture of nitric acid 52%, sulphuric acid 45%.

3. The so-called potato shovels, made entirely of wood.

4. In the Austrian method of cellulose nitrate manufacture (G. MacDonald, "Arms and Explosives," 1909, p. 38) raw cotton is immersed in an acid mixture forty-eight hours, then placed in running water four to eight weeks until free from acid. In the French method, cotton is immersed in an acid mixture for one hour and then dipped in running water for one hour. The remaining acid is subsequently neutralized by a solution of potassium carbonate.

This system of manufacture offers many advantages over other methods of cotton nitration, among which may be mentioned:

(1) The displacement process takes the place of the processes of dipping, digesting in pots, acid centrifuging, immersing and hydro-extraction.

(2) The actual dipping of the cotton is a much less laborious operation—the heavy labor of squeezing out the acid is done away with, while the absence of fumes makes the work much less disagreeable and more healthful. Fuming by this process is almost unknown, and injuries to workmen from acid splashing very infrequent.

(3) Loss of nitrocotton due to decomposition in the digesting pots and acid centrifugals and consequent inconvenience and danger to workmen from nitrous fumes are done away with, and the heavy loss from breakage of pots and lids avoided. The experience of two and a half years at Picatinney and three and a half years at Waltham Abbey have shown that the earthenware pots are very lasting.

(4) The fumes incident to loading and unloading acid centrifugals and immersing are avoided.

(5) The quantity of acid lost is much reduced, and this reduction means less pollution of the discarded wash-waters.

(6) The recovered waste acid is much cleaner, a point of great importance from the point of view of revivification and concentration.

(7) The mechanical loss of nitrocotton in the acid and water centrifuging processes and in the immersing processes is avoided.

(8) A more thorough preliminary washing is obtained with an expenditure of about one-fifth of the quantity of water, and less boiling, with consequent consumption of steam, is required in order to reach a given standard of purity.

(9) Great saving in power is gained by the abolition of the acid and water centrifugals, and in the reduction in the quantity of water which has to be pumped.

(10) Renewals of plant and repairs to plant and buildings are said to be exceedingly low.

(11) The number of hands employed for any given output is much less—the total cost of labor being reduced by two-thirds.

(12) The yield is improved. At Waltham Abbey it is given as 170% (probably theoretical). At Picatinney with a 12.6% nitrogen it is understood that the yield exceeds 155%.

(13) A more stable nitrocotton, of more uniform nitrogen content, is stated to be produced. It is also far cleaner and contains notably less mineral matter.

(14) According to G. Lunge<sup>1</sup> the loss of concentrated acid is only 14% of the weight of cellulose nitrate as compared with a loss of 150% by the older processes.

Sulphuric acid being by volume less expensive than mixed nitrating acid, A. T. Cocking takes advantage of this fact<sup>2</sup> in an attempt to reduce the cost of operating the displacement process. The pertinent points in his patent is to run in sulphuric acid containing about 2% nitric acid onto the nitrated cotton as soon as the nitrating acid has been drained off, no water being admitted. After the sulphuric acid has uniformly saturated the nitrated cotton, it is gradually replaced by water as in the original process, a larger volume of more concentrated spent acid being thereby obtained.

It has long been known that the air in the cotton filament canal offers a certain appreciable resistance to the penetration of the acid, and it has been reasoned that removal of that air from the individual fibers would result in a more uniform nitration and more stable ester. The mechanics of this reason has been embodied in a recent patent,<sup>3</sup> where the nitrating vessel is cylindrical in form and provided with an air-tight cover. Two acid reservoirs which can be either evacuated or placed under pressure are connected with the nitrating vessel. The pipe from one enters the bottom of the nitrating vessel, passes up the center, and delivers its acid at the bottom of the vessel just beneath a perforated false bottom. The cotton having been placed in the vessel, air is withdrawn from it by evacuating one of the acid reservoirs. The cock communicating with the other reservoir is then opened, the acid flows into the evacuated nitrating vessel, and allowed to continue when the cock is closed and the acid which has been in contact with the cellulose sucked off into the other reservoir. This process is alternately repeated, the advantages claimed being that a very much more uniform nitration of the cellulose is thus obtained.

Where it is desired to automatically transport the nitrated cotton from the centrifugals to the wash-house, the hydraulic guncotton conveyor of Selwig & Lange, as shown in Fig. 13, may be used. It is erected close to the nitrating centrifugal<sup>4</sup> and consists primarily of an aluminum or earthenware funnel 250 mm. wide, into which water enters through an opening below the upper rim in sufficient quantity

1. Z. ges. Schies-Sprengstoffw. 1, 2-4.

2. E.P. 16676, 1906. The process of C. Claessen (D.R.P. 200292, 1906) is similar. In this, after the nitration is finished and the acid has been separated, sulphuric acid is injected into the rotation drum of a centrifuge containing the nitrated material, and the sulphuric acid subsequently displaced by water.

3. C. Crépelle-Fontaine, F.P. 397707, 1908.

4. U.S.P. 638647, 1899.

(400–500 l. per minute) and at regular pressure. The funnel is connected below by a siphon-shaped elbow-pipe to a slightly inclined pipe also 250 mm. wide, while to the top of the conveyor is fitted a fume hood from which the acid fumes are drawn by the exhauster.

After being squeezed out, the nitrated material is removed by means of tongs from the centrifugal to the conveyor, where it meets with a

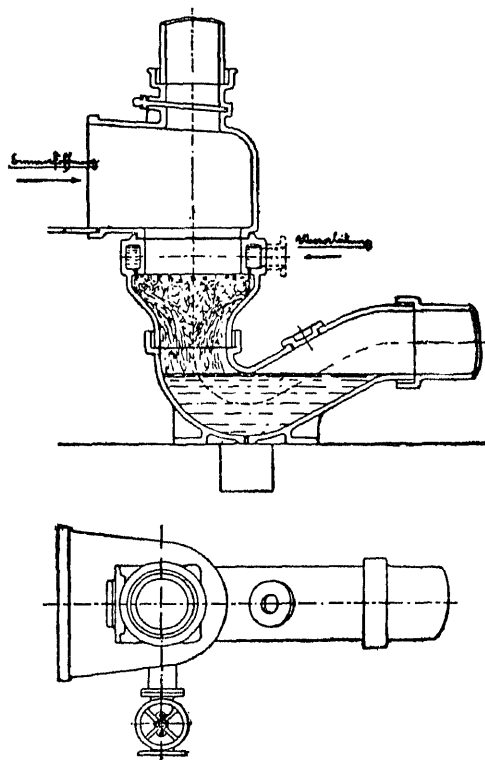


FIG. 13. —Selwig & Lange Guncotton Conveyor.

sufficient stream of water, which transports it through the conveyor pipes in any desired direction.

Generally each conveyor pipe discharges into a tank with perforated false bottom for the collection and preliminary washing of the nitrated material, otherwise the conveyor pipes from several apparatuses may be all connected with one outflow pipe and discharge into a common receptacle.

The guncotton conveyor, in addition to being used for the hydraulic transportation of nitrated material wrung out of the acid centrifugal,

may also be used for the transportation of material which has already undergone preliminary washing.

**Nitration of Paper.** The nitrating apparatus of R. Schüpphaus and M. White, G. Mowbray, Tribouillet and de Besancle and Hyatt, were all designed for the nitration of tissue paper. It has repeatedly been asserted that the finest quality of lacquer and bronzing liquids, transparent plastics and pyroxylin for the preparation of cinematographic and other continuous films, can be obtained only by the nitration of tissue paper. It is a fact that the lightest colored lacquers, the so-called "water-white" grade, are to-day produced in the United States from nitrated tissue paper (so-called paproxyl) in preference to the higher grades of cotton. The actual advantages observed are ease in nitration and speed of penetration, the paper being seldom thicker than 0.003 inch; facility of solution of the nitrated paper; entire absence of cloudiness of the filtered solutions; and the near approach (tintometrically) to forming colorless solutions. It has been pointed out in several works and scientific articles that the high cost of tissue paper must of necessity preclude its use in any large quantities for this purpose, but all, so far as the author is aware, of the manufacturers of pyroxylin plastics in the United States, either manufacture or use large quantities of nitrated tissue paper. When the relative cost of a high grade of cotton is calculated as compared with tissue paper at the present day, it is evident that the difference in cost of raw material is not so marked. The ease and completeness with which solid particles may be removed from nitrated paper solutions of is great importance in the use of this material for continuous photographic films, where freedom from specks is absolutely necessary on account of the high magnification to which the film is subjected when thrown upon the screen.

In the manufacture of a suitable paper for this purpose, the Diamond Paper Mills and other manufacturers are obliged to exercise great care in locating their plants, to insure that the water supply is soft and practically free from organic matter, so that the paper may absorb little or no color from percolation through leaf mold and other decaying vegetable matter.

Of the less important processes, that of R. Schüpphaus and M. White<sup>1</sup> (Figs. 14, 15) consists of a cage *B*, with a central perforated cylinder, intended to insure the rapid and efficient saturation of the tissue paper used for nitration. The patentees claim that with their apparatus no stirring is required, which could only be true with nitration at low temperatures, and not with a temperature of 50–60°. Their

1. U.S.P. 406597, 418237, 1889.

method consists in nitrating the paper in the cage *B*, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the

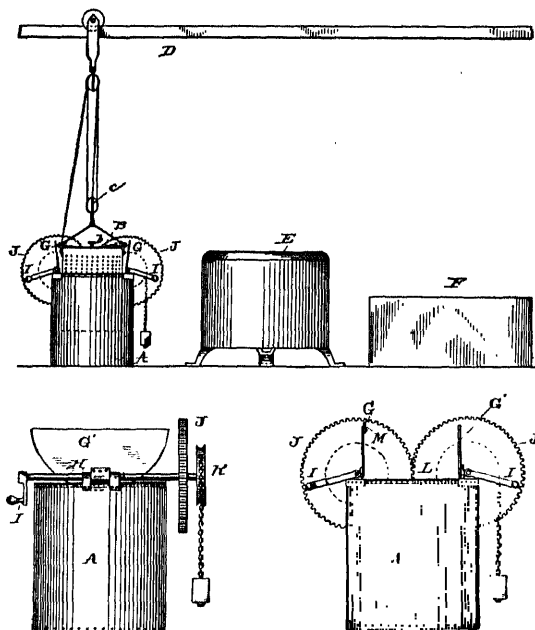


FIG. 14.—Schüpphaus & White Method of Paper Nitration.

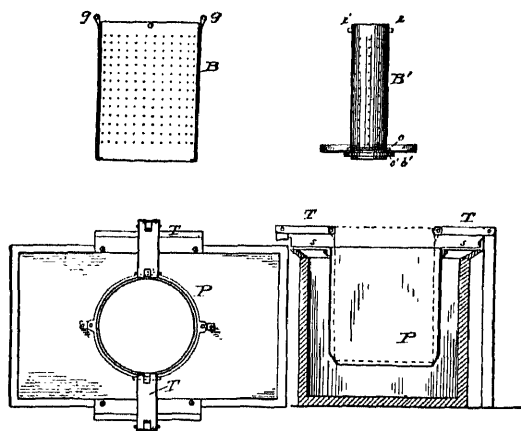


FIG. 15.—Schüpphaus & White Method of Paper Nitration.

internal cylinder *B'*. After nitration the cage goes to the wringer *E*, Fig. 14, of which it forms the basket, the acids then being removed. The cage is next taken to the plunge tank *F*, where the paper is

removed by simply pulling out the central perforated cylinder *B'*. The lower cut shows the nitrating pot with automatic cover, the plunge tank *F* being shown in section and plan.

The method of G. M. Mowbray,<sup>1</sup> now chiefly of historical interest, is perhaps the most elaborate process of tissue-paper nitration which has gone beyond the experimental stage, no paper being nitrated by this method at the present day. The paper lengths shown in the various sectional drawings (Figs. 16 and 17), are entirely imaginary, as

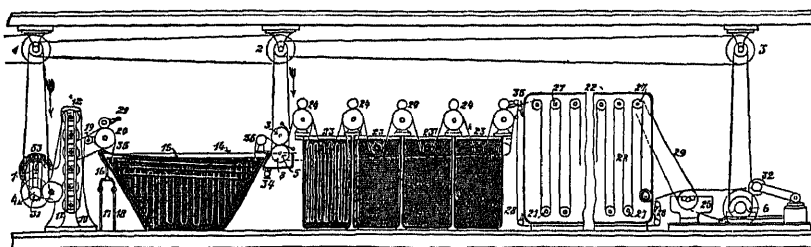


FIG. 16.—Mowbray's Paper Nitrating Apparatus.

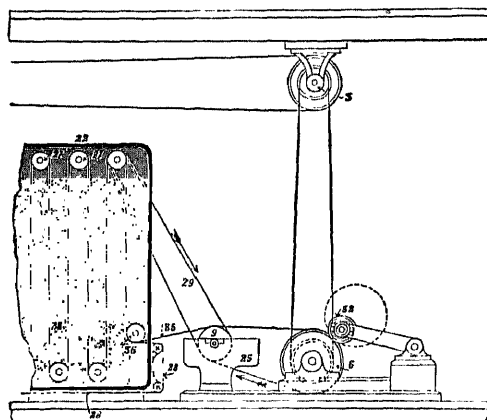


FIG. 17.—Mowbray's Paper Nitrating Apparatus.

the paper upon entering the nitrating fluid would immediately fall to the bottom of the receptacle. He allows the paper web to remain in the acid tank for twelve to twenty minutes, then as the first portion is drawn forward a fresh section takes its place. How to maintain the temperature and strength of acid in the nitrating tank is not stated and is one of the important problems. This method was tried

1. U.S.P. 350497, 350498, 1886; 434287, 443105, 1890; J. France has described methods of using cotton cut so fine as to be practically dust, for the preparation of soluble (U.S.P. 420445, 1890) and insoluble (U.S.P. 420446, 1890) nitrocellulose.

commercially at the plant of the American Zylonite Company, at North Adams, Mass., but was shortly after abandoned.

The paper nitrating apparatus of V. Tribouillet and A. de Besanle<sup>1</sup> consists of a receptacle shown in Fig. 18, comprising a nitrating box with hood. The paper or cotton to be nitrated is first dried at 100°, and either ground or disintegrated, the latter operation being performed in the vessel *A* (Fig. 18), which is 7–8 in. deep and mounted on a bottom-cooling jacket *B*, traversed by a stream of water. To protect the operator from fumes each unit is surrounded by a glass cover *V*, which at least must be unhandy. The nitrating acid consisting of 3 parts sulphuric (sp.gr. 1.834) and 2 parts concentrated nitric containing nitrous acid in solution is used at a temperature of 40–60°. A high yield has been claimed. Claessen<sup>2</sup> describes a method of producing an alcohol-soluble cellulose nitrate, especially suitable for celluloid manufacture, and prepared by acting upon 100 gm. cotton with 3 k. nitrosulphuric acid at 40–50°. The nitrating mixture containing 19% water (limit 18–20%), 42% sulphuric acid (limit 35–46%) and 39% nitric acid (limit 35–45%) is allowed to act

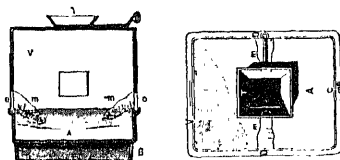


Fig. 18.—The Tribouillet & Besanle Nitrating Apparatus.

for two hours, the temperature not being allowed to rise above 50°. After nitration, washing with cold water is followed by treatment with weak soda solution, then with water again and finally dried. The product contains 9.5–10.5% N, and is said to be readily soluble in 96% alcohol. In polarized light the fibers appear greenish-yellow. To prepare celluloid it is recommended to combine 100 k. of the above cellulose nitrate with colophony 30 k. and 60 k. of 96% alcohol. Instead of colophony, ceresin which gelatinizes in 96% alcohol may be used.

**Hyatt's Paper Nitration Process.** The foregoing described methods have been superseded, at least in the United States, by the process of John W. Hyatt, which although now over thirty years old, is used to-day in essentially the same manner as first brought out by the inventor. With the exception of unimportant modifications and modern refinements in the way of increasing the yield and greater percentage of acid recovery, the process stands to-day alone for the commercial preparation of nitrated tissue paper. So far as the author is aware, the manufacturers of pyroxylin plastics in the United States

1. U.S.P. 216474, 1879; E.P. 5057, 1878; D.R.P. 6828, 1879.

2. D.R.P. 163668, 1904.



at the present time use or produce nitrated paper by methods based upon this process of Hyatt.<sup>1</sup> The process is divided into the four steps of "disintegration," "conversion," "desiccation," and "ablution." This method, upon which tissue paper nitration is at present carried out, is considered of sufficient importance to give in detail, in substantially the words of the inventor:

The first step of the process has for its object the preparation of vegetable fiber for rapid conversion into nitrocellulose, and to this end the improvement consists in taking paper (unsized and uncalendered tissue-paper is best) which has been made in sheets, and, preferably, paper made from stock which has been bleached by any of the ordinary processes, and reducing this paper to small flakes; and this is done in practice by taking a roll of such paper, mounting it in frame, and feeding it between rollers and under tension to a cylinder armed with hook-teeth, set close together, which tear the sheet of paper into exceedingly minute shreds or particles ("flakes"), presenting almost as much edge as surface, so that when immersed in the acids they are acted upon almost instantaneously throughout, and converted more uniformly than would otherwise be practicable. This first step of the process is designated "disintegration," to express the reduction of the tissue paper into minute flakes.

To expedite the converting action still further, the second stage consists in preparing the acid bath, which is placed under a shaft carrying on its lower end a stirrer, and rapidly rotating the shaft, so that the stirrer will give the bath a swift swirling motion; and by setting the blades of the stirrer at an angle somewhat similarly to the blades of a propeller, the centrifugal motion of the acids is increased, crowding them up at the side of the vessel and leaving a depression at the center, so that the flakes of paper being fed into the bath are first swept into the vortex of the swirl by centripetal force, and there subjected to the intensified action of the bath, and as the increasing mass of flakes is saturated and immersed it is gradually swept from the center to the side of the vessel, where its motion is slower, leaving the center free for the reception of the fresh flakes, which are constantly fed into the vortex, where they are acted upon on all sides instantaneously. In this way the treatment of a much larger quantity of the paper is effected than the bath would otherwise act upon effectively. This second step of the process is designated "conversion," to express the transition of the disintegrated flakes from their normal condition into that of saturated soluble fiber.

The quantity of flakes which can be properly fed into the bath,

1. U.S.P. 210611, 1878.

and properly acted upon, as described, having been thoroughly converted, the workman raises the stirrer out of the vessel, which has been resting upon a turntable, and brings under the stirrer another vessel, which meanwhile has been supplied with acids pumped up through pipes, arranged in proper relative position to have the vessel brought under them by the rotation of the turntable. He then lowers the stirrer into this freshly charged vessel, sets it in motion, and feeds in fresh flakes, as before and, when they are converted, again raising the stirrer, passes the vessel onward by the turntable.

The next stage of the process is the separation and recovery of the surplus acid from the saturated soluble fiber, and this is effected as follows: close to the turntable and near to the acid-supply pipes a centrifugal machine is placed, provided with a second perforated rotating removable basket, fitting loosely within the ordinary perforated basket, which latter is mounted upon a vertical shaft, carrying a driving pulley upon its lower end. The acids pass through the perforations in the baskets into the space between the outer basket and the casing, and off through a pipe leading from the bottom of this casing to the reservoir below, from which they may be again pumped up through the supply pipes.

The turntable having brought the vessel containing the acid and converted fiber opposite the centrifugal machine, the vessel is lifted and its contents emptied into the centrifuge which, rotating rapidly, throws out the surplus acid, as is well understood. This third stage is designated "desiccation," to indicate the removal of the surplus acid.

The next stage is to wash out the acids left in the desiccated fiber after the operation of the whizzer; and to this end a washing vat is arranged, supplied with water, and having an overflow near the top, and an inclined table extending from the whizzer to the edge of the vat, so that by lifting the removable basket out of the whizzer with suitable lifting-hooks the desiccated fiber is dumped on the table and slides down into the washing-vat, where it is stirred and thoroughly washed in the constantly changing water until the acids are thoroughly removed. This fourth stage is designated "ablution," to express the transition of the nitrocellulose from the condition of desiccation to the condition of hydrated soluble fiber. From this vat the hydrated soluble fiber may be transferred to another whizzer, which will remove the surplus water, or to a beating-engine, and ground into pulp.

A hood or canopy is provided extending over the entire apparatus, and having an induced upward draft through it, whereby the fumes

from the acids are not only prevented from becoming diffused throughout the room, but are so rapidly carried off through the hood as to greatly relieve the workmen immediately about the apparatus from the distress incident to the use of such acids in open vessels.

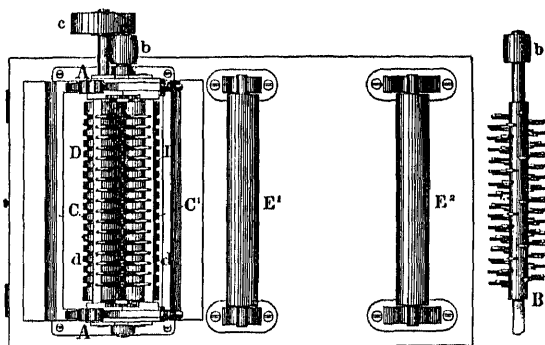


FIG. 19.—Hyatt Tissue-paper Nitrator. Top view of disintegrating apparatus.

The converting vessels are also provided with lugs above and below the center of gravity, and rig-lifting apparatus at the proper points for elevating and tilting the converting vessels to empty them into the whizzer; and by the use of these devices and of a suitable lifting-

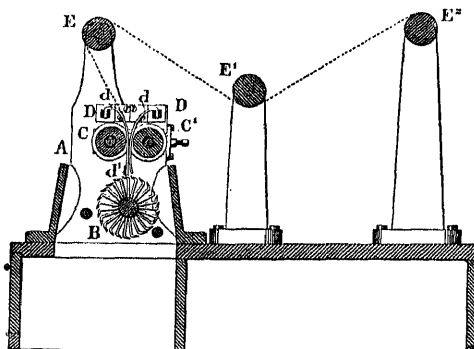


FIG. 20.—Hyatt Tissue-paper Nitrator. Vertical longitudinal section through Fig. 19.

hook for raising the removable basket from the whizzer, the process is conducted with very little occasion to touch the vessels with the hands.

In the drawings (Fig. 19) is a plan or top view of the disintegrating apparatus; Fig. 20, a vertical longitudinal section through the same; Fig. 21, a plan view, showing the general arrangement of the con-

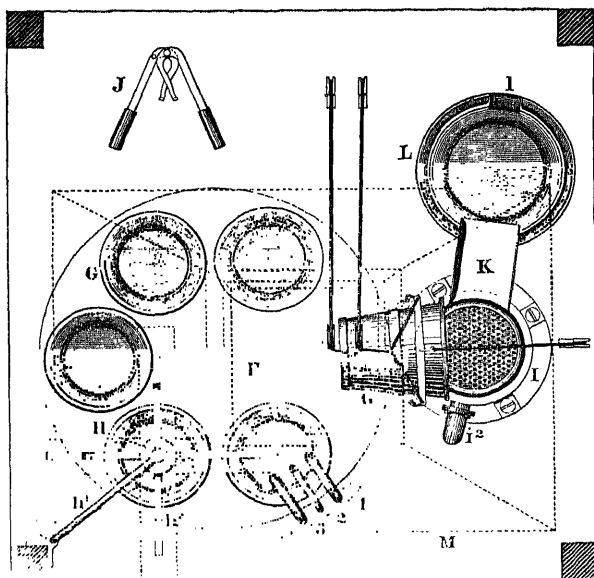


FIG. 21. Hyatt Tissue-paper Nitrating Apparatus. Plan view showing converters

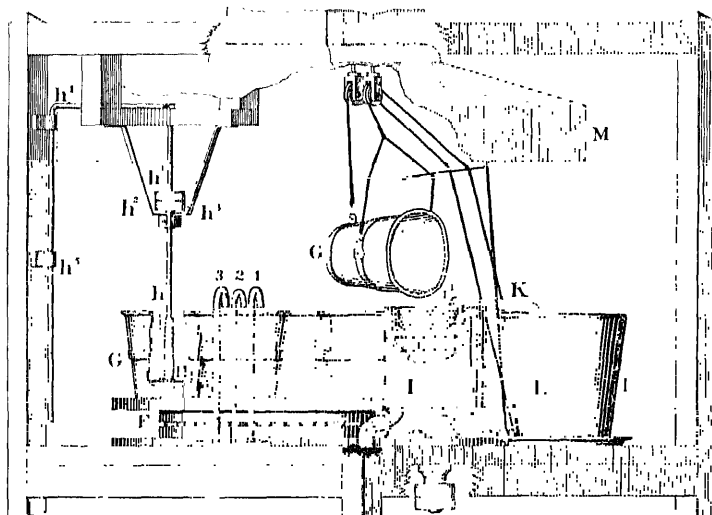


FIG. 22.—Hyatt Tissue-paper Nitrator. Side view of Fig. 21.

verting apparatus; and Fig. 22, a side view, in elevation, of the same.<sup>1</sup>

1. The disintegrating apparatus consists of a frame supporting a pair of housings *A*, with bearings below for the shaft of the disintegrator *B*, and bearings in adjustable boxes above for the grooved feed-rollers *CC'*, a driving-pulley, *c*, being mounted on the projecting end of the shaft of the feed-roller *C*, which roller rotates the feed-roller *C'* by frictional contact. The housings also support a transverse frame, *D*, in which guide-teeth *d*, of wire, are so arranged that each of them shall take into one of the grooves of the feed-rollers.

The guide-teeth, which fit in the grooves of the roller *C*, extend down below the feed-rollers, and are secured to and support the guide-bar *d'*, parallel with the roller and immediately above the teeth of the disintegrator, in line with the line of contact of the feed-rolls.

The teeth which fit in the grooves of the roller *C'* are slightly curved at their lower ends, so as to turn away from the bar *d'*, and the lower points of these teeth are about in line with the lower edge of the guide-bar.

As the feed-rollers are rotated the paper is carried down between them and between the teeth, in such a manner that while the teeth in the roller *C'* permit the paper after it passes below them to turn toward the knives, the guide bar *d'* sustains it against the action of the knives and holds it smooth throughout its entire width, so that it is uniformly fed under the tension of the rollers and presented to and acted upon by the teeth of the disintegrator and reduced to substantially uniform flakes, instead of being irregularly torn and wadded.

The disintegrator *B* consists of a number of hook-teeth or knives arranged close together in spiral lines around and upon its shaft. The elements which will determine the size of the flakes are a given number of teeth and a given rate of speed in the disintegrator, and a relatively slower rate of speed in the feed rollers; but it was not found desirable to reduce the paper to flakes of less size than, say, one-sixteenth of an inch.

The revolution of the disintegrator is in a direction opposite to that of the driven feed roller, and is imparted by a pulley, *b*, on the projecting end of the disintegrator shaft.

The paper is supplied to the disintegrator from a roller *E*<sup>2</sup>, and passes under a roller *E*<sup>1</sup>, and over a roller *E*, down to and between the feed rollers *CC'*. (See the dotted line in Fig. 20.)

The flakes fall into a receptacle below the disintegrator, from which they are removed as required.

The converting apparatus is arranged as shown in Figs. 21 and 22, and comprises first, a turntable *F*, mounted on spherical balls or other suitable suspension, and having such diameter as will accommodate a series of the converting vessels *G*. At a proper point supply pipes 1, 2, 3, leading from the acid reservoirs below, have their spouts curved over, so that one of the vessels *G*, standing upon the turntable, may, by the rotation of the table, be brought under the spouts and charged with acids by the action of a pump. The further rotation of the turntable then moves the charged vessel from the spouts around underneath the stirrer *H*, which is supported above the turntable, so that the charged vessel on the turntable will stand under it centrally. This stirrer is composed of a series of short blades, set or bent at a slight inclination to their shaft, so that they will induce a swirling motion in the acid bath, and attached to the lower end of a vertical shaft *h*, which can be raised high enough above the turntable for the vessel to be placed under or removed from beneath it, and lowered so as to rotate in the vessel near the bottom. This raising and lowering of the stirrer is effected through a bent rod *h*<sup>1</sup>, connected with the upper end of the shaft *h*. The shaft *h* of the stirrer passes through a depending bracket *h*<sup>2</sup>, and is provided with a loose pulley and a fast pulley *h*<sup>3</sup> *h*<sup>4</sup>, through which, when the stirrer is lowered so that the pulleys are brought together, the stirrer is rotated by a belt, the motion being stopped, however, when the shaft is raised and the fast pulley *h*<sup>4</sup> removed from the action of the belt. A pin passing through the rod *h*<sup>1</sup> and resting upon a bracket, *h*<sup>5</sup>, sustains the stirrer when raised. It will of course be understood that the blades of the stirrer and so much of its shaft as is liable to be reached by the acids should be made of or covered with copper or other metal or composition which will resist the corrosive action of the acids, and

It has been said that when Hyatt utilized the relation of camphor to pyroxylin he laid the foundation for an art, and when he devised a satisfactory process of paper nitration whereby transparent objects hitherto unattainable could be produced in large quantities and including the imitations of ivory, mosaics, coral, and amber, he laid the foundation for a "fine" art. It is understood that the proportions of nitrating acids found satisfactory by Hyatt is in the ratio of 50 cc. nitric (sp.gr. 1.47), 100 cc. nitric (sp.gr. 1.36), 100 cc. sulphuric (sp.gr. 1.84) and 18 gm. finely shredded tissue paper, immersed at a temperature of 55° for one-half to one hour, the paper increasing in weight by about 40% during the nitration. The size of the individual pieces is a

the same precaution should be observed in protecting all the surfaces of the apparatus liable to be attacked and impaired by the acids.

The stirrer being lowered into the charged vessel *G* and set in motion, and the acids having been brought to the proper swirl, the flakes of the disintegrated paper are fed into the vessel at or near the center or vortex of the swirl, and subjected to the action of the bath, this stirring operation being continued until, by the action of the acids, the flakes have been thoroughly converted into nitrocellulose. The flakes fed into the center or vortex are, by the operation of the stirrer blades, thrown outward toward the side of the vessel, and their place is supplied by fresh flakes fed in at the center until the thickness of the mass indicates the limit of the saturating capacity of the bath, when the shaft of the stirrer is raised and the turntable rotated, carrying the vessel from underneath the stirrer round opposite a whizzer or centrifugal machine, consisting of the case *I*, firmly secured in position, the perforated rotating basket *i*, mounted upon the upper end of the vertical shaft, by which it is rotated through a pulley on the lower end of the shaft (see Fig. 22), and the removable perforated rotating basket *i'*, fitting loosely within the basket *i*.

To transfer the converted flakes from the vessel *G*, a tackle is rigged between the turntable and the whizzer, with three hooks, two on one rope, to take into the lugs or eyes on the sides of the vessel, and thereby lift the vessel, and one on the other rope, which takes into the lug or eye near the bottom of the vessel to tilt it when raised; and on the opposite side of the whizzer a line is provided, running through the eye to the lifting tackle, so as to draw the raised vessel into proper position to be tilted and emptied into the removable basket of the whizzer. (See Figs. 21 and 22.) The whizzer meanwhile having been duly set in motion, the surplus acid is rapidly expelled from the converted flakes, and passes down between the outer basket *i*, and the case of the whizzer to a pipe *i'*<sup>2</sup>, which conducts it to the cistern or reservoir, from which it may be again pumped up through the supply pipes 1, 2, 3. When the action of the whizzer is completed and the converted flakes freed from the surplus acid, the removable basket *i'* is lifted out by means of a pair of internal lifting hooks, *J*, 4, and its contents dumped upon the inclined table *K* and into the washing vat *L*, which is supplied with water, and the converted flakes are stirred and washed therein, under a constant circulation of water, supplied in any suitable manner and passing off through the overflow *l*, near the top of the vat. From this vat the washed mass is removed for further treatment not pertaining to this process, which is concluded with this condition of the hydrated soluble fiber.

It will be observed that the diameter of the turntable is such as to allow space for a series of the converting vessels *G*, the relative position of which is such that while one is in readiness to be lifted and its contents dumped into the vessel, another is being charged with acid, and a third is beneath the stirrer, while between the one under the stirrer and the one at the whizzer there is room for several others, so that there may be always a series of vessels that have passed the stirrer, ready for being dumped into the whizzer and passed again under the supply pipes, and the operation may be thus carried on without any intervals between the stages.

matter of adjustment of the shredding machine, that produced to-day being about  $\frac{1}{2}$  to 1 in.<sup>1</sup> Ash determinations made by the author on this paper gave results of 0.08–0.12%. J. W. Swan<sup>2</sup> has devised a method of producing cellulose nitrate in a continuous manner by passing cellulose, in the form of a long web, band or sheet of paper, continuously through the mixed acids at such a rate as to allow of sufficient nitration of the cellulose.

✓ **Nitration of Cotton for Cheaper Grade of Pyroxylin.** For uses in combination with oils and pigments, in opaque products, especially in pyroxylin coating compositions, where the solubility, viscosity, and freedom from insoluble particles is of no great moment, a grade of cellulose nitrate is made by means of centrifugals, which is used in enormous quantities. The following is the process in its essentials:

The acid mixture consists of sulphuric acid 55%, nitric acid 17%, water 28%, total acidity 72%. The initial temperature of the nitrating acid is 46–48°,<sup>3</sup> time of nitration fifteen minutes, and five wringers nitrated each two hours. The heat of reaction raises the centrifuge contents to 54–57°. Yield 128–135% on the weight of the dry cotton. Nitrogen content 12.35–12.40%, nitrating mixture 50 times the weight of the cotton. The product is nearly soluble in commercial wood alcohol, contains considerable residue, has a thin flow, and dissolves very readily. The stability is often low. As the temperature of nitration increases, the cost increases correspondingly, for the hotter nitrating acid means a more fluid pyroxylin, more loss in washing and neutralizing, more frequent replacement of rubber gloves, etc., and greater frequency of the batches fuming in the wringer. The value of this grade of pyroxylin lies in the small amount of solvent necessary to make a workable solution, and this is of especial value in the imitation leather industries, where the solvent is not recovered. Raising the sulphuric acid in the mixture lowers the nitrogen content of the pyroxylin; raising the nitric acid increases the percentage of nitrogen in the nitrocotton. Elevation of temperature without changing the compositions of the nitrating mixture has but little effect on the nitrogen content, although the yield may be diminished.

**Pyroxylinum.** Under this general name a cellulose nitrate soluble in alcohol and ether is official in the Pharmacopœias of Belgium, Brit-

1. Analyses made by the author of that grade of paper pyroxylin most suitable for lacquers gave nitrogen 11.0–11.2%, ash 1.0%, KI starch test at 65°, about 15 minutes; temperature of ignition 170–175°.

2. E.P. 21729, 1894; abst. J.S.C.I., 1895, 14, 1062.

3. The temperature of the acid upon coming in contact with the cotton. It has to be heated higher to allow for cooling during transmission of the acid to the centrifuge.

ain, Finland, Galicia, Germany, Greece, Helvetia, Italy, Netherlands, Portugal, Russia, Spain, Switzerland, and the United States. Except Belgium, all the prominent Pharmacopœias give under the word "Colloidium" methods for the preparation of this form of cellulose nitrate, as will be noted from the following table:

Formula.	Brit.	Fin., Ger., Spain, Italy, Neth.	Gal.	Russ.	Swiss.	U. S.
Nitric acid.	50 cc.	400 gm.	500 gm.	8 gm.	9 gm.	1,400 cc.
Sulphuric acid.	50 cc.	1,000 gm.	1,000 gm.	20 gm.	18 gm.	2,200 cc.
Cool the mixture to		20° Ger. 20-25° F.	30° F.	20° F.	15-20° F.	32° F.
Weight of cotton.	10 gm.	55 gm. dried at 100° (Italy).	55 gm. dried at 100°.	1 gm.	1 gm.	100 gm.
Macerate in nitrating acid.	3 min.	24 hours at 15-20°.	24, 36, or 48 hours at a temp. of 35°, 25°, 15°.	24 hours at 15°.	15-24 hours.	Until sol. in ether-alcohol.
Dry.	Over water-bath.	In the air or not over 25°. Not over 80° (Neth.)	In free air.	at 25°.	At gentle heat.	Not above 60°.

The Greece, Spain and Portugal Pharmacopœal methods direct to stir 20 parts of potassium nitrate to a uniform paste with 30 parts sulphuric acid, sp.gr. 1.84, and put in at 30° (Spain), 1 part dry cotton, allowing the acid to act upon the cotton for five minutes (Greece), ten minutes (Portugal), or twenty-four hours at 20-30° (Spain), then wash out the acids and salts with boiling water (Spain), until all the acids and sulphates (Spain) have been removed, when the nitrated cotton is dried in the air. In another method, 29 parts sodium nitrate is mixed with 66 parts sulphuric acid, sp.gr. 1.84, 2 parts of cotton immersed and allowed to remain in the nitrating mixture for 8 days, after which it is washed to neutrality and dried.

Irrespective of the method of formation, the finished ester must be neutral, dissolve completely in ether containing ethyl alcohol with but little residuum, and leave practically no ash upon ignition.

**Pyroxylics of Low Nitrogen Content.** Much experimental work has been recorded in endeavors to reduce both the cost and inflammability of cellulose nitrate products by introducing the minimum amount of nitric acid into the cellulose molecule which will at the same time produce esters of physical properties commercially valuable. Knecht<sup>1</sup> has described unstable cellulose nitrates prepared by treating cellulose with nitric acid of varying strengths (sp.gr. 1.1-1.415), the neutralized products containing 3.0-35.8% nitric acid in combina-

1. Ber., 1904, 37, 549; abst. J.S.C.I., 1904, 23, 335.



tion, equivalent to 0.7–8.0% nitrogen.<sup>1</sup> A. Voigt<sup>2</sup> obtained gelatinous products by combining both the nitrating and pulverizing processes in one. He immersed cotton in 97 parts conc. sulphuric acid and 3 parts nitric acid at 2–3°<sup>3</sup> and obtained after neutralization and drying a very fine powder of high stability, which the patentee considers very advantageous for the manufacture of shooting and blasting powders and of lacquers. No statements of solubility, however, are given.

In 1908 B. Herstein<sup>4</sup> patented methods of formation of structureless nitro derivatives of cellulose, insoluble in alcohol, ether, amyl acetate and acetone; containing less than 4.5% nitrogen, and which are transformed into a transparent or translucent mass by the addition of caustic soda. The cellulose in the form of thin paper or cotton is immersed in an acid mixture consisting of about 63% by weight of absolute sulphuric acid, about 10% nitric acid, and the remaining 27% partly water and partly other inert material. This mixture may conveniently be obtained by adding to 85 parts by volume of sulphuric acid 1.66 sp.gr., 15 parts nitric acid by volume of 1.42 sp.gr. As soon as the cellulose is immersed, visible reaction takes place, the entire mass of cellulose loses its structural form, and is converted into a gelatinous transparent magma. It is essential that the acids be cooled to a low temperature (below 20°), in order that the cellulose may not dissolve in the acid mixture, and to insure that it becomes gelatinized merely. After a few minutes' immersion the excess of acid is poured off and the residue repeatedly washed with large quantities of cold water, pressed, and dried at a low temperature. The actual percentage of nitrogen varies materially with the method of manufacture, but is seldom over 4%. The most characteristic reaction of the product is its deportment when brought in contact with caustic alkali solutions, in which it quickly gelatinizes, forming a plastic, transparent mass, readily moldable, and which may be diluted with water and forced through fine orifices. It is readily hardened or coagulated by treatment with weak acids, and combines with phenol, resorcinol, or pyrogallol, the latter property differentiating it from

1. None were entirely gelatinized products, and no statement of their solubilities is given.

2. U.S.P. 855869, 860776, 1907; E.P. 5126, 1904; abst. J.S.C.I., 1907, 26, 780.

3. The scoured and cleaned cotton cellulose is immersed in conc. sulphuric acid at 2–3°, in the ratio of 5 times by weight of acid to cellulose. The fibers rapidly disintegrate with a rise in temperature. After the structure has been destroyed, about 2 k. conc. nitric acid is added, the temperature of the mixture being kept down by artificial means. After two to three hours the mass congeals into a solid cake which is washed out in large quantities of water and dried. Thus prepared the product is a fine powder.

4. U.S.P. 879871, 1908; abst. J.S.C.I., 1908, 27, 353.

true cellulose nitrates. Drs. Jasper E. Crane and C. Joyce<sup>1</sup> have elaborated upon this process and investigated the formula of the derivatives produced and the mechanics of the several reactions. In their preferred method paper cut in small pieces is immersed in a mixture of 65.5% sulphuric acid, 9% nitric acid, and 25.5% water, the ratio of acid to cellulose being at least 100 to 1. The temperature of the bath is kept at 5–10° and 6–12 minutes the preferred period of immersion.<sup>2</sup> After nitration the mass is immediately plunged into cold water, and the lumps or "curds" obtained rapidly washed until neutral. Combustions of the product previously dried *in vacuo* at 50° to constant weight gave results corresponding to a mono-nitrate on a C<sub>12</sub> molecule for cellulose, the yield being about 110%, against 119% theoretical for a mono-nitrate, thus showing considerable loss by solution in the acid.<sup>3</sup> It was found to dissolve in strong acids, strong bases (including trimethylamine), pyrogallol, Schweitzer's reagent, and zinc chloride solutions. The anhydrous product was insoluble in acetic anhydride, but upon the addition of a small amount of water, acetation ensued and a product readily soluble in acetone but incompletely in chloroform resulted.<sup>4</sup> It is evident that these lower cellulose nitrates have valuable possibilities.

**Other Later Processes.** Gaston C. de Brialles of Paris<sup>5</sup> has patented in various countries a process of nitration by means of acids concentrated by electricity. It consists in inserting two platinum poles into the lower portion of a closed vessel in which the cellulose is confined, to make the acid more concentrated by electrolysis, the current being 3–4 volts. The anode is larger than the cathode, both being made of platinum. If the temperature is not below 30° the cellulose is nitrated in three to four hours. It is claimed that the electrolytic decomposition of the water formed in the reaction prevents the liberation of heat which would accompany the dilution

1. J.S.C.I., 1910, 29, 540–542, with bibliography of 18 citations.

2. Decrease in temperature or time lowered the gelatinizing action on the cellulose. Increase in temperature gave buttery products, partially miscible with water and indicating a breakdown of the cellulose aggregate.

3. The sulphur was determined by the method of Hake and Lewis (J.S.C.I., 1905, 24, 376), and nitrogen by the Dumas method in preference to the Lunge nitrometer, the latter giving incorrect and lower results, a proof that the nitrogen is present in the form of nitrate-nitrogen.

4. It contained 2.32% N., indicating it was a completely acetylated derivative of the formula C<sub>22</sub>H<sub>31</sub>O<sub>18</sub>N, similar to the aceto-nitrates described by Berl and Smith (Ber., 1907, 40, 903; abst. J.S.C.I., 1907, 26, 273), and prepared by them from cellulose nitrates of higher nitrogen content. Their increased reactivity with iodine, Fehling's solution and fixation of basic dyes showed the product to contain cellulose hydrates. In this connection see Ost and Westhoff (Chem. Zeit., 1909, 33, 197; abst. J.S.C.I., 1909, 28, 325), and C. Schwalbe (Z. ang. Chem., 1909, 22, 197; abst. J.S.C.I., 1909, 28, 216).

5. E.P. 2902, 1906; D.R.P. 203377, 1906; F.P. 364349, 1906.

of the acid.<sup>1</sup> The method in use at the Stains Company plant in Paris is stated to consist in immersing small strips of fine tissue paper for a long time in conc. nitric acid, after which a small quantity of conc. sulphuric acid is added, and the product washed to neutrality. A. Luck and A. Durnford<sup>2</sup> first change the cellulose into hydrocellulose before nitration. E. Quinan<sup>3</sup> immerses the cellulose in hot nitric acid to dissolve out all mineral constituents, then transfers to a nitrating bath of nitric and sulphuric acid to complete the esterification.

**Washing.** The first operation of eliminating the acid after centrifugalization is washing. This is done in a large wooden tank filled with cold water, which should previously have been run through a sand or other suitable filter. By means of overflow plugs, a continuous stream of water may be allowed to fall over the nitrocotton while the latter is kept in constant motion by means of manual stirring with wooden paddles. After the cotton has been so thoroughly washed that a small piece tastes but faintly acid, the water is allowed to run off through a false bottom, and wrung out in a centrifugal machine, or the last wash water may be allowed to remain in contact with the nitrocotton for several hours in order to wash the acid out from the central canal of the cotton filament. Often the process is so arranged that the nitrocotton is allowed to soak in the last water over night.<sup>4</sup>

It has been stated that the higher the ratio of sulphuric acid to nitric acid in the nitrating acids, the longer the time necessary and the greater the number of changes of water required, before the water from the boiling vat is free from acid reaction. It appears that the lower nitrated cottons are more readily washed free from acid than those of higher nitration. It is pretty well understood that the neutralization of free acids in nitrocotton with ammonia, as in the pat-

1. See also H. Diamanti, H. Champin, P. Loisel, F.P. 377425, 379509, 1906; J.S.C.I., 1907, 26, 1066.

2. E.P. 4760, 1895.

3. D.R.P. 117349, 1898.

4. F. I. DuPont (U.S.P. 724932, 1903; 762757, 1904) has devised a process of purification in which it is intended to more quickly and completely remove the acid from the canals of the nitrocotton by means of compressed air. The material is agitated in water under great air pressure, the pressure suddenly removed, whereby the impurities are more readily washed out. The apparatus is a cylinder with conical bottom, and with pipe and pump connecting the top and bottom to produce violent circulation. An inert gas may be introduced in such a manner as to pass through the nitrocotton. In his U.S.P. 648147, 1900, the idea of dehydration by solvent displacement (F. DuPont, U.S.P. Reissue, 11651, 1898), is extended to the washing of nitrocellulose. The acid nitrate without a preliminary washing is placed in a hydraulic press, the acid squeezed out, water allowed to percolate through the guncotton under pressure, a final alkaline washing being given in the same manner. The patentee claims by this method to be able to reclaim a much greater amount of spent acids with less loss of nitrated cotton, and with practically no liability to loss from fuming.

ented process of H. Anthony,<sup>1</sup> is a dangerous procedure unless the temperature be kept very low, as the experience of C. Weber,<sup>2</sup> the author, and probably others can testify. When a nitrocotton neutralized with ammonia is dried at temperatures above 60° it may explode with great violence. Haddan<sup>3</sup> boils the nitrocotton under pressure, increasing the pressure sufficiently toward the last so that the nitrocotton is reduced to a fine powder, thus obviating pulping.

**Stabilizing.** Originally stabilization was effected simply by prolonged washing in cold running water, followed by a very short treatment with a boiling alkaline carbonate solution. In the manufacture of guncotton in Austria and France to-day, it is stated this boiling process with alkaline carbonates is continued as an important step in neutralization and hence in increasing the stability. The number and length of boilings required varies in different localities and especially with the methods of nitration employed. It has been found that with the displacement process of nitration, stabilizing is much more easily effected than with the centrifugal process.<sup>4</sup> It is still an open question as to the quickest and most efficient method of cellulose nitrate purification. In any process the washing is continued until the desired stability as indicated by heat tests has been acquired. The nature of the water available for maceration of the nitrocotton undoubtedly has much to do with the stability, but experiments are not sufficiently conclusive for accurate generalizations on this point. A great deal of discussion has arisen as to whether washing, and especially the boiling processes, may not be carried too far as regards ultimate stability. The effect of continued boiling, while undoubtedly decomposing the unstable esters, must also have an appreciable effect in breaking down the stable ester itself. It is well known that if a nitrocotton be boiled for a sufficiently prolonged period, the percentage of ether-alcohol soluble matter will rise, and the nitrogen content fall. The breaking down of the ester is accompanied by the formation of obscure acid bodies, which have to be removed to prevent them from reacting upon the stable nitrate.

R. Robertson,<sup>5</sup> who has made experiments on a large scale having

1. U.S.P. 143865, 1873. He neutralized with ammonia and by his process produced a nitrocotton used extensively in photography.

2. J.S.C.I., 1892, **11**, 117.

3. E.P. 5830, 1900. See U.S.P. 210612, 1878, J. Hyatt and J. Jarvis for apparatus for washing paper pulp.

4. Systematic experiments carried out in 1905 at Waltham Abbey (Nathan, J.S.C.I., 1907, **26**, 183) to determine the most suitable and economical purification of nitrocotton, showed that in the displacement process, the number and length of boilings could be materially reduced, as compared with the ester prepared centrifugally. (For reasons see Thomson "Displacement Process").

5. Chem. News, 1906, **94**, 9.

for their object the best means of obtaining a pure and stable nitro-cotton by boiling, finds that for the elimination of impurities and rapid attainment of a stable product, boiling in dilute acid at the beginning of the process is superior to an alkaline treatment, and has the additional advantage of tending to prevent undue hydrolysis of the ester itself. He found that the acid hydrolysis must not be unduly curtailed or elimination of the impurities will be rendered difficult. The importance of retaining a certain degree of acidity in the first boiling is as important, as it is disadvantageous to prolong the latter boilings. As a result of his investigations the method of a series of long initial (acid) boilings followed by a series of short (neutralizing) boilings is recommended. It appears to be pretty generally recognized that alkaline boilings in nitrocellulose neutralization interfere with temporary and permanent stability.

Various processes have been suggested from time to time, in which stability may be increased or made more permanent. The suggestions have either (1) increasing stability by the introduction of an antacid, or (2), detection of acidity in the product after manufacture. Of the first subdivision, R. C. Schüpphaus<sup>1</sup> was apparently among the first to devise a process of this nature, in which he recommends the addition of urea in methyl- or ethyl- alcohol solution, after the nitro-cotton has been freed from all but traces of acid by washing. Skoglund<sup>2</sup> patented ammonium oxalate and carbamate, and more recently completely substituted ureas<sup>3</sup> as 5% diethyldiphenylcarbamide. Cyanamide, dicyanodiamide, tricyanotriamide<sup>4</sup> and salts of dicyanodiamidine<sup>5</sup> have also been claimed as efficient. Luck and Cross<sup>6</sup> as the result of their observations upon the nature and properties of the impurities eliminated in the stabilization of the cellulose nitrates under the action of diluted solvents, found that these solutions, when freed from dissolved cellulose nitrate, contained acid bodies which readily unite with metallic bases, as lead oxide, forming insoluble compounds. Upon this, they have based a process of stabilization consisting in digesting the nitrate with a 1% solution of lead acetate or zinc chloride at 80–100°, and after thirty to sixty minutes' heating, the excess of solution is removed and the nitrate thoroughly washed until entirely free from soluble metallic

1. U.S.P. 514830, 514838, 1894; E.P. 22384, 1893;  $\frac{1}{2}$ –2% being recommended. See "Stability of Pyroxylin Plastics," Chapter XIV.

2. E.P. 18362, 1888.

3. C. Claessen, U.S.P. 909546, 1908; E.P. 16725, 1906.

4. E.P. 27515, 1903; abst. J.S.C.I., 1905, 24, 44.

5. D.R.P. 205762, 1905. Addition to D.R.P. 201215.

6. U.S.P. 647420, 1900; E.P. 18868, 1898.

salt.<sup>1</sup> Mercuric chloride, which has been added to guncotton to raise the stability test, it has been found, does not increase, but rather masks the test.<sup>2</sup>

To detect the development of acidity in this ester after manufacture, the addition of small amounts (usually less than 0.5%) of various bodies to the nitrate before drying has been tried. Rosaniline base, diphenylamine base, and litmus and blue archil<sup>3</sup> among other things, have been tried. Carneiro, as the result of extensive tests<sup>4</sup> of diphenylamine, concludes that it cannot be considered as a stabilizer for smokeless powders. Rosaniline, when used in small amounts, has no visible effect on the cellulose nitrate, but upon the development of acidity, small, dark-colored patches appear in the gelatinized powder, and this darkening is not caused by small particles of iron held mechanically in the ester from the apparatus used in purification. Diphenylamine is probably the most used at the present time in amounts of about 0.45% calculated on the weight of cellulose nitrate. It is dissolved in the ether used to convert the nitrocotton into the colloid.

**Pulping.**<sup>5</sup> On completion of the boiling or stabilizing process the wet pyroxylin is transferred to a beating or pulping machine quite similar to that used in paper mills for pulping the raw material used in the manufacture of paper. The Cyrus Carrier pulper (Fig. 23) consists essentially of a wooden tub, in which revolves a large roller containing steel blades set in iron heads. This roller revolves over a bed knife of steel plates, by which action the contents of the tub is shredded into pulp. The desired fineness is determined by rubbing a small sample of the pulped mass in the hand, spreading out on the palm and examining for fineness, or the mass is pulled to pieces between the fingers, the hands being held toward the light, and the length of the fibers which project from each side as they are torn apart being also an indication of the thoroughness of comminution. In still another method a small amount of the hydroextracted pulp is shaken up in a large bottle, the fineness being judged from the appearance. After the nitrocotton has reached the required degree of fineness, valves in the bottom of the vat are opened, the contents passing to settling tanks, where the water is allowed to run off. This

1. The product of the treatment contains about 2% of the basic oxide (PbO) in combination with the nitric acid group.

2. S. Thomas, *Z. ang. Chem.*, 1898, **12**, 1003, 1027; *J.S.C.I.*, 1898, **17**, 1179.

3. E.P. 2430, 1871, E. Nicholson and A. Price.

4. *Z. ges. Schiess- u. Sprengst.*, 1909, **4**, 29.

5. The proper purification of nitrocotton on a manufacturing scale involves difficulties which can be properly appreciated only by those experts directly engaged in the process.

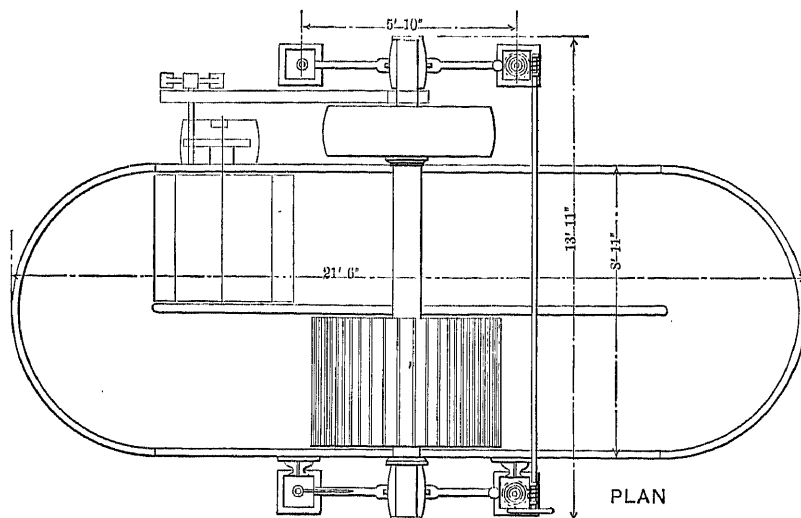


FIG. 23.—Currier Pulper and Refining Engine.

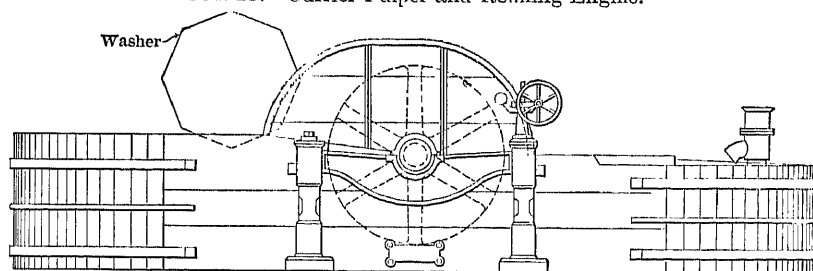


FIG. 24.—Currier Pulper and Refining Engine.

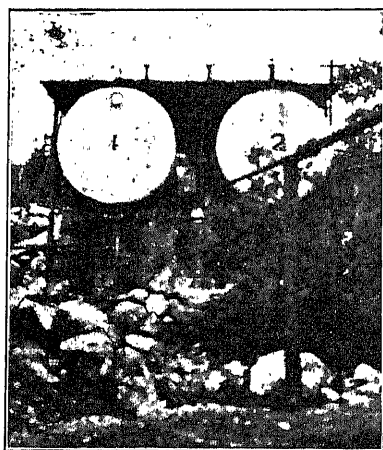


FIG. 25.—Nitrating Acid Storage Tanks.

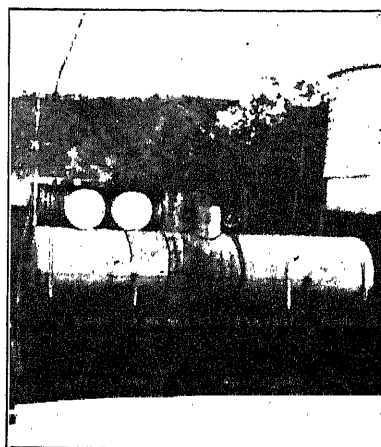


FIG. 26.—Nitrating Acid Storage Tanks.

engine is fitted with a washing device whereby the excess of dirty water is removed during the period the contents are being pulped. The mechanism consists of an octagonal-shaped drum with perforated brass sieve, inside of which are buckets which take up the water and deliver to a central trough and thence discharge to an outside vat.

This firm also builds an "Auxiliary Refining Engine" (Fig. 24), which takes the nitrocotton from the pulper and reduces it to any fineness required in much less time than the regular pulper. This auxiliary refiner consists of an iron revolving disk with steel blades on both sides. This revolves between two other blades, one on each side, and by the action of the revolving disk the material is ground to the fineness required. To adjust the fineness, the two stationary plates may be brought closer together by means of a screw gear operated by the handle on the outside of the machine. The parts are interchangeable, the front and back plates and disk being replaceable. Excessive pulping increases the solubility of guncotton in ether-alcohol, while long treatment with even such feeble alkalis as calcium carbonate tends to hydrolyze cellulose nitrate.

Since the introduction of the very thorough system of purification by boiling, the original process of pulping as patented by J. Tonkin,<sup>1</sup> and three years later by F. Abel<sup>2</sup> has not the importance as a purification process as formerly. However, there is no doubt that with a long staple cotton the long tubes contain impurities which are best and most readily removed by disintegrating the individual fibers, and pulping not only reduces the length of the fibers by breaking, but crushes them as well, so that impurities may be removed mechanically as well as by solvent action.

**Removal of Foreign Bodies.** After pulping, it is often advantageous to treat the nitrocotton in some manner in order to remove from it any particles of metal, grit, or similar foreign bodies. The nitrocotton suspended in a volume of water may be run through what is called grit traps, placed at convenient intervals in a long shallow trough the bottom of which is covered with blanket. In general the foreign bodies are much heavier than the nitrocotton and fall to the bottom by gravity, where they are intercepted by the blanket fibers. An electromagnet placed in the last trap removes any particles of iron

1. E.P. 320, 1862.

2. E.P. 1102, 1865. Of the several important improvements introduced by Abel the chief is the process of pulping. Having traced the cause of instability in nitrocotton to the action of nitric acid on resinous and waxy substances contained in the cotton fiber, he succeeded in their elimination by long boiling, thorough washing and pulping the cotton in poachers. The first attempts of von Lenk to effect purification on a manufacturing scale by prolonged immersion of the nitrated cotton in running water was unsuccessful even after eleven weeks' treatment.



or steel. It is said that some factories use a "knotter," a contrivance to remove small knots or any large pieces of nitrated cotton imperfectly pulped. If the cellulose nitrate is to be used for lacquers or artificial filaments the thorough filtration which it undergoes removes all foreign particles. If for smokeless powder, filtration of the colloid cake through the "macaroni" press, as described in Chapter XVIII, is supposed to remove all extraneous matter.

**Poaching.** In some factories the nitrocotton is washed during the pulping by means of drum washers attached to the beating engine; in others the washing is done in separate vessels called "poachers." These usually hold about 100 lb. nitrocotton for each 110 gal. capacity, and are agitated by power-driven paddles. The nitrocotton receives from 3-7 washes in this apparatus, being allowed to settle after each washing. The wash water contains fine particles in suspension, the removal of which increases the stability, and in the case of the earlier waters, often a scum forms on the surface containing nitro bodies of low stability.

**Blending.** Although poaching has in a great measure blended the nitrocotton, still the solubility and viscosity of the cotton has to be brought to a definite standard, depending on the commercial use for which it is intended.<sup>1</sup> After the nitrocotton has been neutralized, viscosity and solubility determinations are made, from which the use of the cotton for a desired purpose is calculated. By the admixture of various batches in certain proportions, the physical properties of solubility, viscosity, and clearness may be duplicated from quite dissimilar nitrocelluloses.

**Centrifugal Dehydration.** But a small percentage of the nitrocottons used industrially is dried before use. In using it in the moist state, there is not only a saving in time between manufacture and use through elimination of the drying process, which at the low temperature required (30-35°) takes several days, but the danger in handling and use is materially diminished where the nitrocotton is continually moist, and in the majority of countries the transportation of nitrated cotton is prohibited except in very small quantities

1. In E.P. 14690, 1907, A. Liedbeck describes a process for producing a uniform nitrocotton by allowing the beating and nitration to proceed simultaneously. The acid mixture is introduced into a beater which is then set in motion, the cellulose being introduced by degrees through a feeding aperture in the hood, until the whole quantity weighed off has been fed in. When the mass has acquired the desired fineness it is freed from acid centrifugally, and neutralized in the regular manner. It is evident that in this process, as described, there must be a large loss of cotton, both by solution in the nitrating mixture and in subsequent washing, while the ratio of acid to cotton must be great in order that the last portion of cellulose immersed may be reacted upon by nitrating acid of practically the same composition as the first portion.

unless in the moist state. The liquid used to eventually replace the water must fulfill two conditions: It must be miscible or nearly so with water and a non-solvent of the nitrocotton, and must also be a constituent normally present in the formula in which it is intended to use the pyroxylin. This narrows the liquids of commercial value to denatured ethyl alcohol and propyl alcohol or the first fractions from fusel oil rectification, consisting mainly of propyl alcohol, and usually miscible with water in any quantity without turbidity.

The usual method after continued washing has resulted in a nitrocotton of acceptable stability, is to wring the nitrocotton and either partially displace the remaining water with the dehydrator in the centrifuge or convey the pyroxylin to a separate apparatus where the displacement of water by alcohol takes place under great pressure. In the former method all of the water which is removable by a centrifuge is wrung out, leaving from 18-30% remaining. If acetone has been used as the dehydrating agent, as suggested by Durnford,<sup>1</sup> the cellulose nitrate is left as a putty-like mass difficult to handle or subdivide. If ethyl or propyl alcohol is employed the nitrocotton can be readily disintegrated by the hand.<sup>2</sup> Alcohol is then sprayed into the centrifuge during motion until the density of the alcohol-water running out of the centrifuge has a given gravity corresponding to a known proportion of alcohol to water, when the spray is turned off and the centrifuge continued until no more liquid is wrung out.<sup>3</sup> The nitrocotton is then ready for use without further treatment. In any dehydrating process the alcohol, of course, is subsequently recovered by careful rectification and used over again.

In the apparatus for alcohol dehydration according to Selwig and Lange (Fig. 27) the basket of the centrifugal has, besides an outer rim, an inner finely perforated one, and a detachable cover of aluminum or bronze for covering the space between the two. In this circular space, which is lined with a cotton sack, the wet gun or collo-dion cotton (122 lb. or 60 k.) is rammed somewhat tightly. The detachable cover is then fitted on, and the drum closed with the tightly fitting lid. A finely perforated pipe is then inserted in an opening in the lid, through which the gunecotton is given a preliminary coating of weak, already used alcohol, which is followed by a second covering of alcohol of the desired strength. Gunecotton treated with alcohol by means of the centrifugal has the same alcohol content (30-33%) as that which has been hydraulically pressed out.

1. E.P. 20880, 1892.

2. See G. W. Gentieu, U.S.P. 931749, 1909.

3. Another method is to continue spraying until the alcohol issuing from the centrifuge is of the same strength as the entering alcohol.

The output of a centrifugal is said to be about 600 k. of wet gun-cotton in ten hours, and depending on the diameter of the centrifuge basket.

On the same principle as the Thomson displacement nitrating methods<sup>1</sup> a process of displacement by dehydration has been worked out in England. In order to replace the water (left in nitrocellulose after washing) by alcohol, without the use of pressure and in such a manner that a very small amount of dilution of the alcohol with water takes place, the nitrocellulose is first covered with water so that practically all air is excluded. Alcohol is then quietly run down the sides of the vessel so as to form a layer on the surface of the water. A

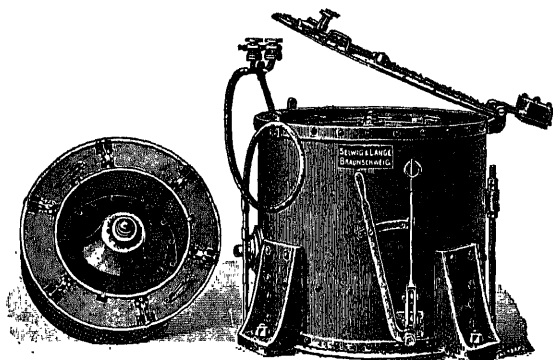


FIG. 27.—Selwig & Lange Centrifugal Pyroxylin Dehydrator.

cock at the bottom of the vessel is slightly opened, so that the water slowly flows away at a rate of fall of level in the vessel of half an inch to one inch per hour. The alcohol flows in and replaces the water in the interstices of the nitrocellulose, the treatment being continued until all the water has been displaced by alcohol. When dehydration has thus been completed, the excess of alcohol is removed by pressing or centrifuging.

In order to prevent the centrifuged nitrocotton from sticking to the sides of the wringer, a rope may be placed around the sides of the interior of the basket, and by loosening the rope after centrifugalizing, the contents is readily removed. Of less labor, however, are the hydroextractors arranged with bottom discharge, as that made by the Tolhurst Machine Works, Troy, N. Y., and shown in Figs. 28 and 29. The extractor does not differ from the usual type, except the foundation is so constructed as to allow a truck to stand under the extractor.

1. F. L. Nathan, J. M. and W. T. Thomson, E.P. 7269, 1903.

After the water has been whizzed out of the material, the lid is raised, and the load falls down into the truck, thus doing away with the necessity of shoveling it out.

**Dehydration by Hydraulic Pressure.** Fig. 30 represents a cross-section of a hydraulic pressure dehydrator as built by Cyrus Currier's Sons, Newark, for the late Petrifoid Co., and is a repre-

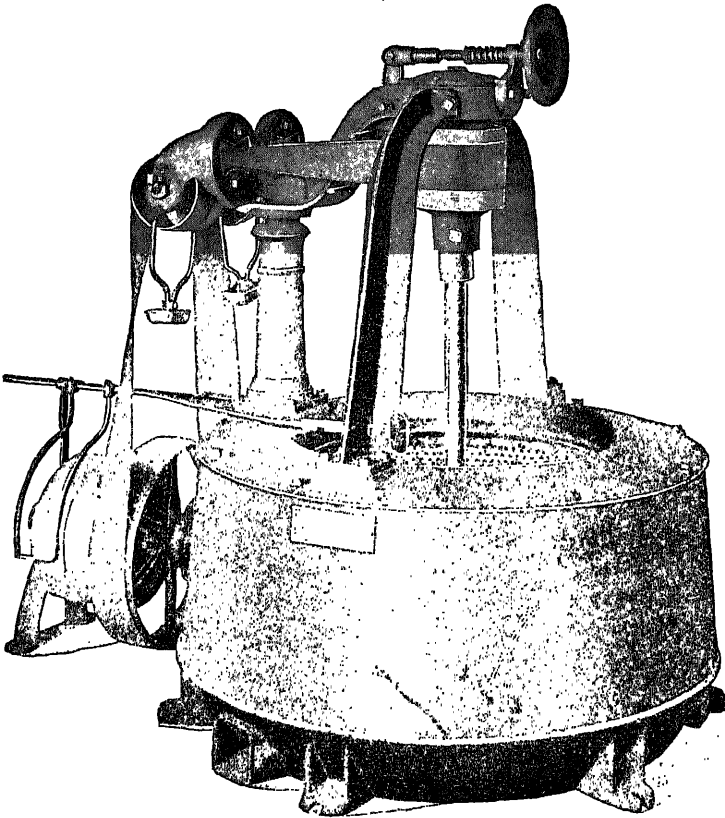


FIG. 28.—Tolhurst Hydro-Extractor Arranged with Bottom Discharge.

sentative apparatus for dehydration by pressure. It is known as a "Two-plunger Hydraulic Dehydrator," the nitrocellulose being placed in cylinder *B* when the bottom is closed by the action of the ram in the cylinder *C*. This forces the perforated bottom up against the lower part of cylinder *B*, which communicates the pressure to the mass in *B*, by means of the force of the plunger actuated from the cylinder *A*. As the plunger descends and pressure is brought to bear on the

mass in *B*, the water is forced out and through the perforated bottom *D*, through the tube *E*, and into a receiving receptacle. After sufficient pressing the perforated bottom *D* is lowered, by the action of the plunger in the cylinder *C*. Pressure is then placed on the dehydrated mass from the plunger in cylinder *B*, the contents being forced out in one cake in the form of a cheese. Afterward the plunger *A* is drawn into the cylinder *A*, and the process repeated. By means of a series of 4-way hydraulic cocks, the pistons at *A* and *C* can be raised or lowered at will. If another fluid, as alcohol, is to displace

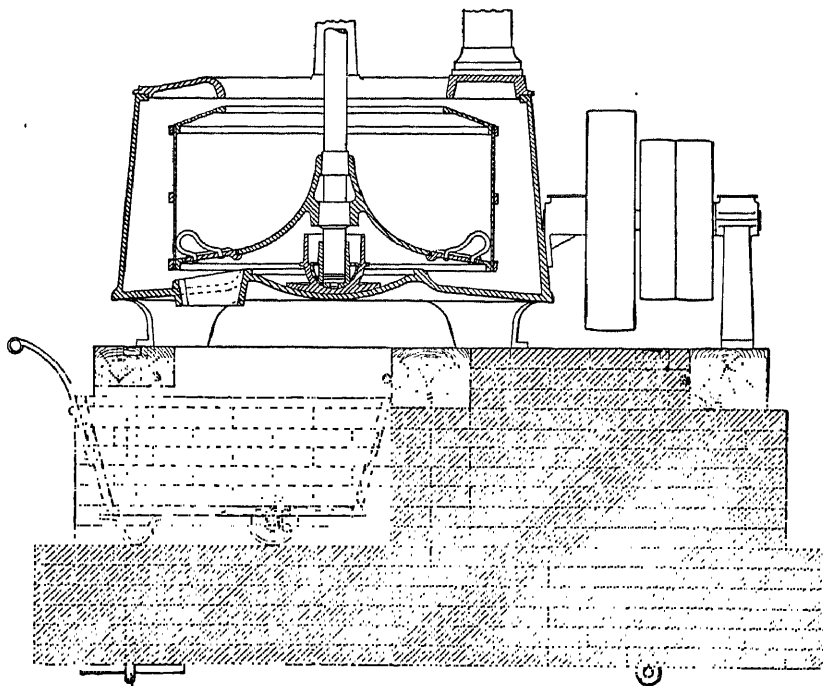


FIG. 29.—Sectional View of Fig. 28.

the water remaining in the pressed cheese before expulsion of the latter, the piston in *A* is drawn up, and by means of a funnel the required amount of alcohol is introduced. When the latter has entirely permeated the cheese by gravity, as indicated by the first drops coming out of *E*, the operation of pressure is repeated, except in this instance the fluid obtained is led to settling tanks and thence to a still to be rectified. With a dehydrator of the dimensions as shown, the cheese obtained weighs about 17 lb., of which 20–22% is fluid.<sup>1</sup> The

1. See also "Hydraulic Nitrocotton Press," F. I. DuPont, U.S.P. 648147, 1900;

maximum pressure which is obtained by means of the accumulator is 2,000 lb. per sq.in. The time required for placing the nitrocotton in the press, driving out the water and alcohol displaced, is about twenty-five minutes;  $2\frac{1}{2}$  gal. of alcohol is required, of which nearly one-half gal. remains in the cheese, and at least another gallon is recoverable from the mixed water and alcohol, when rectified as described in Chapter V.

In pyroxylin lacquer manufacture for the preparation of imitation leather and water-proofing effects, where pressure dehydrated nitrocotton is used, each formula is usually calculated on the basis of 25% alcohol in each pound of cellulose nitrate used. See also the hydraulic dehydrators described and illustrated in Chapter XVIII, under Smokeless Powder Manufacture, the pyrocollodion described there—except for its high viscosity—being suitable for lacquer manufacture.

**Drying.** If it is desired to reduce the amount of moisture in the nitrated cotton to 2-3% it may be spread on wooden cloth-covered frames,<sup>1</sup> in small detached wooden houses. Warm air at a temperature

E.P. 15693, 1897; A. Durnford, E.P. 20880, 1892; "Modern Hydraulic Gun-cotton Presses," C. Grau, Z. ges. Schiess-u. Sprengstoffw., 1909, 3, 321, 382 (13 figures); also J. Hyatt, U.S.P. 280745, 1883; 296967, 1884.

1. According to Guttman, this process is objectionable because the nitrocotton is thereby completely insulated, and there is danger of an electric charge, especially with elevated temperatures. To obviate this apparent danger he suggests that copper plates be provided for drying, having conical apertures of  $\frac{1}{4}$  mm. diameter on top and 1 mm. on the bottom, thus rendering it impossible for them

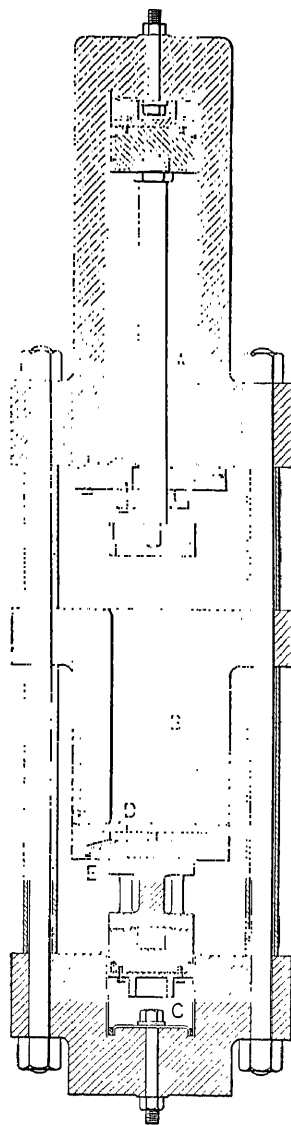


FIG. 30.—Carrier Two-Plunger Hydraulic Dehydrator.

not exceeding  $40^{\circ}$ <sup>1</sup> hastens the removal of the moisture, the air having been previously dried.<sup>2</sup> The uniformity of heat in the dry-house has much to do with the stability, which decreases with increase of temperature and moisture. The danger of drying nitrocotton may be partially avoided by treating the latter with alcoholic calcium chloride solution after alcohol dehydration, corresponding to 1–2% of calcium chloride on the weight of cellulose nitrate. In celluloid and artificial leather manufacture this amount of calcium chloride would seldom interfere with the finished products.<sup>3</sup> In the Volney method of drying<sup>4</sup> the cellulose nitrate is placed in a closed vessel and dry, heated air or inert gas introduced. A certain portion of the air is then removed from the vessel in order to reduce the pressure, the temperature being kept constant at  $35\text{--}40^{\circ}$ . These processes are alternately repeated, the pressure in the drying vessel fluctuating about 10%. For quick drying, the Quinan apparatus,<sup>5</sup> it is claimed, is being used in Cape Colony with satisfactory results. This apparatus is a shallow basket some 4 ft. in diameter, with the bottom of fine wire gauze. On this is laid a sheet of cheese-cloth on which is spread a layer, about  $2\frac{1}{2}$  in. thick, of wet nitrocellulose, which has been made as granular as possible by being rubbed through a sieve. A cover of silk cloth of fine mesh is placed in position over the nitrocellulose, to prevent any material being carried away by the current of hot air. This drying basket fits tightly on top of a circular support, into which a current of hot air is led, and thus passes through the nitrocellulose. When drying has been completed, a current of cold air is passed through the apparatus to cool the charge before removal. After drying, the nitrocotton is transported to various parts of the factory in wooden- or tin-tared containers, and with tightly fitting covers.

The Emil Passburg drying chambers, as built by the J. P. Devine Co., Buffalo, are designed for the drying of nitrocellulose rapidly at a low temperature by means of reduced atmospheric pressure

to be clogged by the nitrocotton. To prevent friction the plates may be covered with leather on the edges, and are connected with each other by metallic strips which are carried into the ground. This arrangement renders an accumulation of electricity in the nitrocotton improbable, any electricity developed being carried into the ground.

1. C. T. Tyrer, *Pharm. J.*, 1898, 109, and Mowbray, U.S.P. 349659, 1886, places the temperatures at  $32^{\circ}$  and  $38^{\circ}$  respectively, as the maximum with which nitrocotton may be dried with safety.

2. J. Edison recommends cold, intensely dry air, maintained slightly above the freezing point (U.S.P. 249600, 1881). See F. G. DuPont, U.S.P. 516924, 1894, and E. Bronnert and T. Schlumberger, E.P. 1858, 1896.

3. F. G. DuPont, U.S.P. 712406, 1902.

4. U.S.P. 874265, 1907; see also J. W. Hyatt, U.S.P. 297935, 1884; J. E. Bousfield, E.P. 5076, 1901.

5. E.P. 22783, 1906.

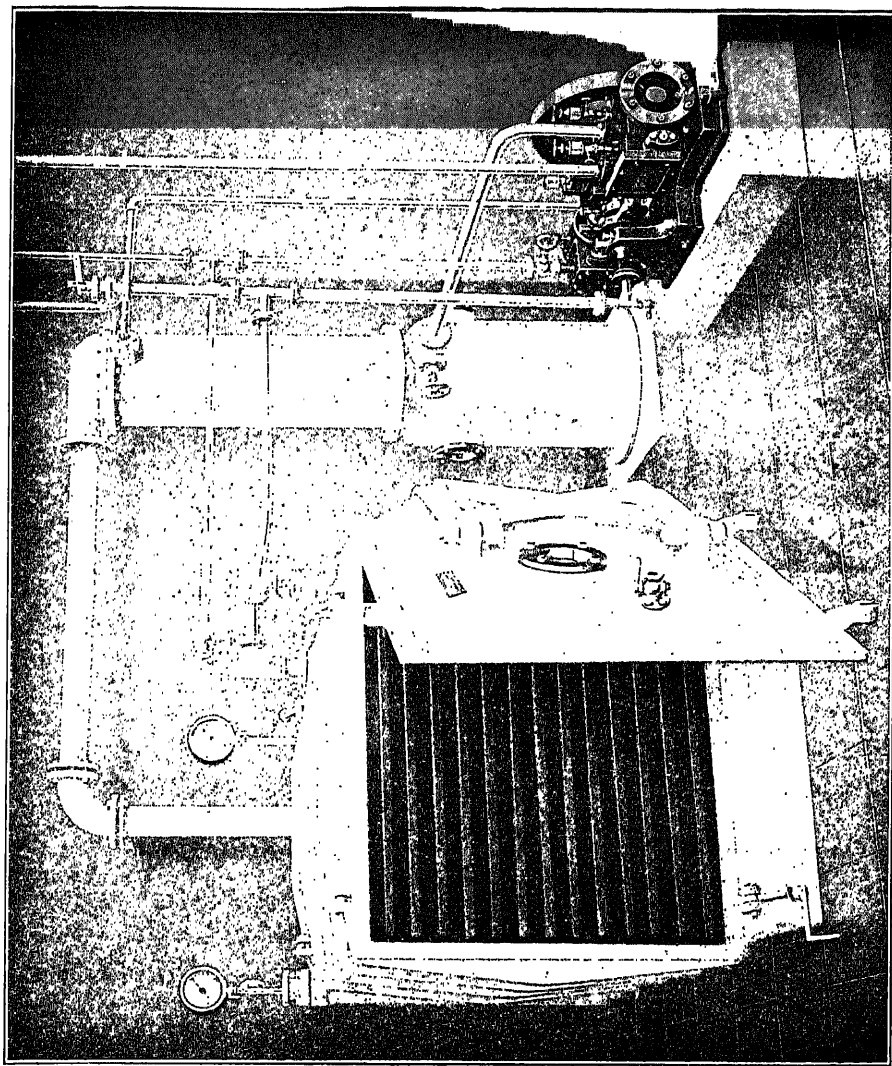


FIG. 31.—Emil Passburg Patent Drying Chamber (J. P. Devine Co., Buffalo, N. Y.).



(Fig. 31). The dryer consists of a cast- or wrought-iron chamber or cylinder, hermetically closed at one or both ends by large doors. It contains a number of steam- and water-tight heating shelves or pipes placed one above the other through which steam or hot water is circulated to produce the required degree of heat, which may be as low as 17°. The material to be dried is placed on these shelves in trays of suitable size and shape. The apparatus in Fig. 32 is provided with an expansion chamber and other safety devices to receive, in case of explosion, the expanding gases, and thereby decrease their destructive power. These gases have first to destroy the vacuum in the expansion chamber before they can exercise any pressure on the sides of the apparatus. Any excess pressure then opens the safety valves and apertures to admit of free escape of gases. In case of extraordinary pressure the whole back of the chamber, which is held in position by springs only, will be forced open, thus affording immediate relief.

**Fortification and Acid Recovery.** After nitration, the spent acid—richer in water and poorer in nitric acid—is usually run by gravity into storage tanks and allowed to cool before being purified or fortified. Restoration of used acids is usually comprised in three steps as follows:

- (1) Elimination of impurities (cotton and nitrated cotton) in suspension.

- (2) Removal of nitrogen oxides.

- (3) Increasing the nitric and sulphuric acids therein to a given strength.

- (4.) Mixing used and unused acid to form a new nitrating mixture. In practice (3) and (4) are practically one series of operations.

In addition to varying proportions of oxides of nitrogen in solution, the spent acid contains small amounts of cotton fiber in suspension, which it is desirable to remove before reuse. These are eliminated mechanically, by filtration through acid-washed sand, or shredded asbestos filters, or a filter composed of highly nitrated cellulose, usually cotton. In the method of F. Pool<sup>1</sup> the mixed acid is agitated with naturally occurring barium sulphate (barytes, heavy spar) which is practically insoluble in the acid mixture, and after thorough stirring of the barytes in the acid, it is allowed to subside, carrying with it the insoluble filaments. Filtration through a fine mesh platinum sieve has been recommended, but the author is unaware of the method having ever been used. In the Thomson displacement method of nitration there is but little cotton in suspension in the used acids,

1. U.S.P. 251938, 1882; J. Hyatt and F. Pool, U.S.P. 274335, 1883; M. Lefferts, E.P. 24, 1883.

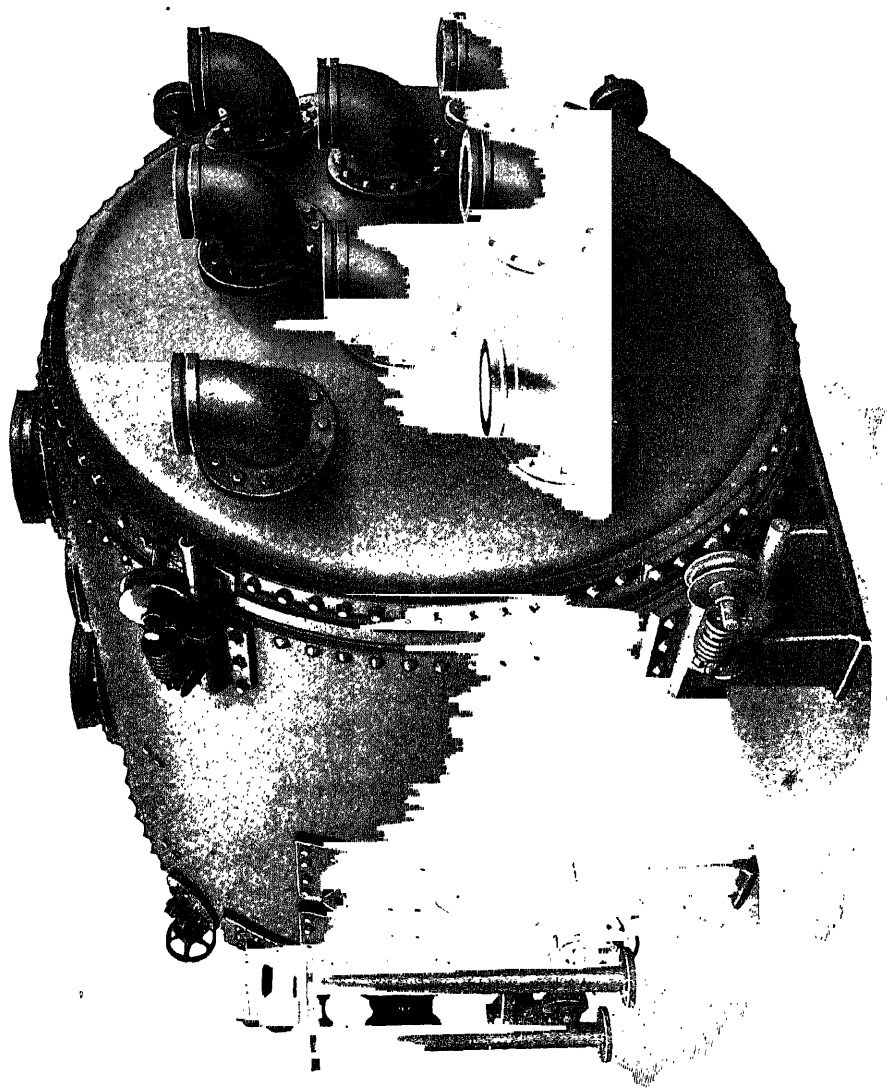


FIG. 32.—Passburg Safety Vacuum Drying Apparatus for Fulminates and Nitrocellulose.

due to the fact that they are so gradually removed from the nitrated cellulose that the latter acts as a filter to retain all fine, solid particles.

The removal of nitrogen oxides is accomplished in several ways. In one method compressed air is blown through the spent acid, thus driving the gases out of solution, which are led through condensing towers of brick or volcanic stone and into weak alkali solution, forming nitrates useful as fertilizers. Another plan is to eliminate the oxides by gentle heating of the mixed acid, but nitric acid is also volatilized. Aspirating cold air through the spent acid is tedious and not always successful, and calls for previous drying of the aspirated air. Physical absorption with pumice stone has been disappointing. A system of aëration in which the spent acid in a thin stream is allowed to meet a heavy blast of air has apparently not fulfilled the claims of the inventor, due to the weakening of the spent acid, if the volume of air was increased sufficiently to eliminate all the oxides. The amount of nitrogen oxides present, in the majority of instances, is less than 1%, and in many nitrating houses is not eliminated.

To guard against accidents from leaking valves or corroded pipes, the spent acid is usually left in the storage tanks until shortly before use, these tanks being located by gravity so that in event of leaks from valves or pipes no acid will run out.

The degree which the nitrating acid has been weakened in nitric acid by the process of nitration will depend upon (a) the amount of nitrogen introduced into the cellulose, the higher cellulose nitrates abstracting more nitric acid per unit weight of cellulose; (b) the method of nitration used, there being less loss of nitric acid and oxides in the air with the displacement method than with the processes of hand, pot, or centrifugal nitration; (c) the extent of "fuming" in the individual nitrations, the greater the fuming (i.e., liberation of nitric oxides) the weaker the spent acid in nitrogen.

The method of fortifying by the addition of a crystalline nitrate (usually potassium nitrate) and depending on the sulphuric acid to liberate nitric acid *in statu nascendi*,<sup>1</sup> has been discarded on account of interference by the large amount of potassium sulphate formed by the interaction of the sulphuric acid on the nitrate. The use of nitrates soluble in water, the sulphate of which is insoluble (calcium, strontium, or barium nitrates) proved unsatisfactory, as it introduced another operation, that of filtering off the precipitated sulphate, and another expense is introduced into the process from the additional amount of sulphuric acid required to unite with the base.<sup>2</sup> A fortified

1. F. Pool, U.S.P. 306519, 1884; 336822, 1886.

2. F. Pool, U.S.P. 343850, 1886. The most elaborate and expensive system

acid usually consists of (a) the maximum of used acid which, when combined with (b) sulphuric acid either 98%, or sulphuric acid 98% containing amounts up to 30% sulphur trioxide (oleum),<sup>1</sup> and (c) a mixture of nitric acid 50–60% with sulphuric acid 45–35%, or less often (in the United States) nitric acid 98%.<sup>2</sup> The composition of the spent and fortifying acids having been obtained analytically, they are mixed in certain proportions to produce the desired mixture, one method of mixing which has been found satisfactory for large-scale nitration being as follows:

Three tanks are arranged at such a height that their contents will flow by gravity into the weighing-tank scales, and thence into the nitrating house. The spent acid is pumped into one of the storage tanks (see Fig. 26), the other two containing the sulphuric acid and the nitric acids respectively. Of the various mixing scales in use, in the United States those of the Fairbanks Co. of New York shown in Figs. 33 and 34, has proven satisfactory, both in delicacy, freedom from attack by acids, and length of life, but also on account of their simplicity of action. By means of pipes connecting the weighing scales with each tank, the required amounts of each acid are weighed in separately, and by means of a stirring arrangement connected with the interior of the scales the contents is slowly but thoroughly stirred for a considerable time (about three-quarters of an hour) to insure complete mixing. A sample is then withdrawn and subjected to analysis, any further adjustment of strength being made in the manner just described. From the scale tank the acid is run into the nitrating centrifugals or pans by gravity as required, or another storage tank may be provided, in which instance a day's supply ahead can always be kept. Nitrating houses and fortifying houses are usually arranged on a hillside if possible, in order to take advantage of varying heights for gravity flow of acids. The acid tanks ("eggs") are usually constructed of high carbon iron, the Bessemer steel tanks of G. Mowbray having apparently not come into use.

In F. DuPont's apparatus for making mixtures of nitric and sulphuric acids<sup>3</sup> the retort in which the nitric acid is generated is connected to an absorber containing sulphuric acid by circulating

of nitrating acid fortification is probably that of J. Hyatt, F. Pool, J. Everding, J. Stevens, and W. Wood (U.S.P. 299388, 1884), designed for handling large quantities. It has been estimated that its equipment and installation would cost at least one hundred thousand dollars.

1. R. Schüpphaus (U.S.P. 526752, 1894; E.P. 18683, 1894; abst. J.S.C.I., 1894, 13, 1220) was the first to patent the strengthening of nitrating acids by the use of sulphuric anhydride. It is a question to be ascertained whether the use of the anhydride is prejudicial in any way to the nitrated cotton.

2. U.S.P. 350498, 1886.

3. U.S.P. 743922, 1903.

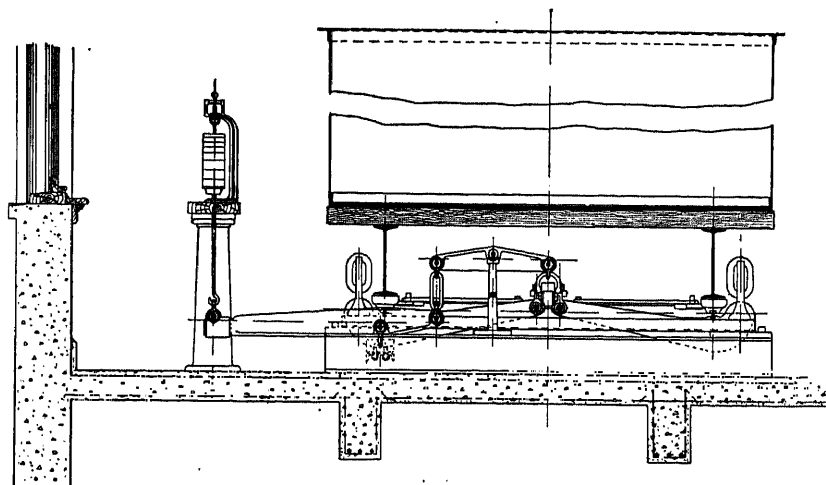


FIG. 33.—Fairbanks Scale.

These scales, shown in Figs. 33, 34, are designed especially for the weighing of corrosive fluids, as nitrating acid. The scales can be constructed so as to admit of mechanical stirring devices in the mixing tank, without impairing the accuracy—which is usually about 5 lb. in a 60000 lb. charge.

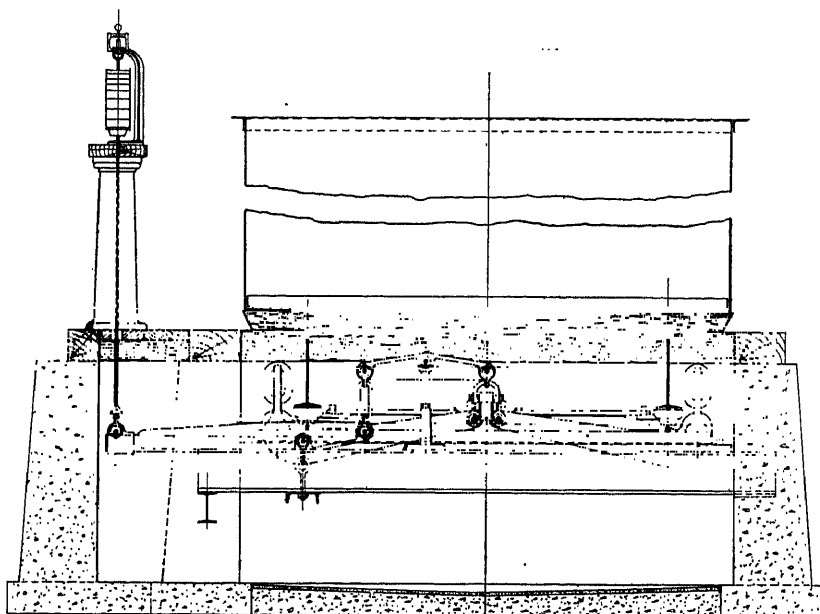


FIG. 34.—Fairbanks Scale.

conduits, one of which conveys the nitric-acid vapor to the absorber, while the other conduit—by the aid of a blower—returns the unabsorbed gases, the absorber being fitted with an agitator. The method of dehydrating sulphuric acid of C. Wilhelm<sup>1</sup> is characterized by tangentially introducing over the surface of the acid, contained in a round vessel, hot gas or air, in such a manner that the concentrating acid takes up a spiral motion toward the center of the vessel, where it is withdrawn, the apparatus comprising a series of such vessels, and provision being made for the escape of the hot gas or air, after taking up the moisture from the acid, directly out without coming into contact with the charges in the other vessels. V. Vender<sup>2</sup> utilizes atmospheric nitrogen in his process of denitrating and recovering acid mixtures suitable for nitration, the oxides of nitrogen being subsequently condensed. A system of two towers may be used, the first of which is heated externally by the hot gases; these then pass through the second tower, which is fed by the acid mixture to be treated, and from the bottom of which strong sulphuric acid is withdrawn. The nitrous gases from the second tower are condensed, and furnish nitric acid of about 60% strength; this is admitted to the first tower, together with a part of the strong sulphuric acid previously obtained, and strong nitric acid (98%) is thus obtained by distillation, the sulphuric acid, reduced to about 75% strength, being sent back to the second tower. All the sulphuric acid and nitric acid are thus recovered in a concentrated form, and synthetic nitric acid is prepared at a reduced cost.

**The Evers Denitration Tower.** When the mixed nitrating acids have become so spent as to make additional fortification unprofitable, or the acid has too much dissolved cellulose and nitrated products in solution, the mixed sulphuric and nitric acids may be separated as by the Evers<sup>3</sup> system of denitration.<sup>4</sup> This comprises a denitration tower divided into three compartments increasing in size from below

1. D.R.P. 176370, 1905.

2. F.P. 405819, 1909; abst. J.S.C.I., 1909, 28, 423. For electrolytic method for renewing waste acids from nitration see Saltpetersaure-Industrie-Gesellschaft, D.R.P. 180052, 1905, and First Addition thereto, D.R.P. 180587, 1906; abst. Chem. Centr., 1907, 1, 1083. E. Neumann (Sprengstoffe, Waffen u. Munition, 1908, 4, Oct. 15) has given a description of the various systems for fortifying and denitrating spent acids and recovery of nitrous gases.

3. D.R.P. 145743, 1903; 182216, 1902. In D.R.P. 176369, 1904, R. Evers describes a method comprising a vessel upon whose bottom are two coils, one within the other, through which steam is to be heated is passed, alternately, so that the heat of the concentrated acid, which passes directly from the apparatus through a short tube set into the wall of the vessel, is given up to the dilute acid to be next introduced into the midst of the vessel.

4. J. Rüdeloff, Z. ges. Schiess- und Sprengst., 1907, 2, 144. This article describes the usual methods and apparatus for denitrating mixed acids.

upward. Each compartment is filled at its upper portion with pieces of earthenware or other filling material, space being left at the bottom, in each case, for collecting the acid, which is then passed on to the next compartment below by an acid distributor. A hot air and steam injector is also fixed at the base of each compartment. At the top of the tower is the supply chamber, similarly fitted with injector and distributor. Air and steam are introduced at a temperature of not less than  $400^{\circ}$ , and the rate of flow is so regulated that they travel with the greatest speed in the lowest compartment and slowest in the top chamber. All organic compounds in the acid are oxidized and a water-white sulphuric acid of  $60^{\circ}$  Bé. obtained, containing only a trace of nitrogen compounds. The condensed nitric acid consists of 80% of an acid of  $40^{\circ}$  Bé. and 20% of  $36^{\circ}$  Bé. containing only 0.2–0.3% of nitrous acid. A special apparatus, containing bundles of small tubes, precedes the main condensing apparatus, and is said to yield good results in preliminary condensation.<sup>1</sup>

**The Redpath Method of Acid Calculation.** The following graphical method for the determination of the quantity of fortifying and sulphuric acids to be added to preliminary mixings was communicated to the author by the late Leon W. Redpath, and has never before been published. As devised by him it assumes that the concentration of the various components in the fortifying acid, the percentage composition desired in the final mixing, and the total number of pounds of acid in the preliminary mixing are constant. If the conditions conform to these specifications, the results will be mathematically correct; but should the conditions deviate from these specifications a proportional error will be introduced. However, under working conditions the error so introduced will be within the limits of error allowed for the chemical determination.

The method requires the preparation of two charts. Fig. A determines the effect upon the composition of the preliminary mixing caused by the further addition of fortifying acid.

It is first necessary to make a calculation to determine the effect produced upon the components of the preliminary mixing by the further addition of 1,000 pounds of fortifying acid.

Let  $a$  = the per cent of one component of the fortifying acid.

$b$  = the per cent of that same component as desired in the final mixing.

$c$  = the total number of pounds to be adjusted.

1. In the case of denitrating the acids received from the manufacture of nitrotoluene, a special vessel, U-shaped in cross-section, is placed in the system immediately after the tower, to condense any nitrotoluene carried over, and thus prevent a block in the condensing pipes.

Then

$\frac{a-b}{c}$  = the effect produced upon that component in the preliminary mixing by the addition of one pound of fortifying acid.

For example: If the sulphuric in the fortifying acid has a concentration of 41.8%, and if the concentration of the sulphuric acid desired in the final mixing is 56.50%, and if the total quantity of acid used in the preliminary mixing is 54,000 pounds, then

$$\frac{41.80 - 56.50}{54,000} = -.000272.$$

Or, the addition of 1,000 lb. of fortifying acid would have altered the strength of the sulphuric acid .27%.

The second calculation is made by the same method to determine the effect upon the nitric by the addition of 1,000 lb. of fortifying acid to the preliminary mixing.

Assuming that the nitric in the fortifying acid is 52.40%, and that 28.2 is desired in the final mixing, then  $\frac{52.40 - 28.20}{51,000} = .000416$ ,

which will be the effect upon the nitric of the preliminary mixing by adding 1 lb. of fortifying acid to it. The addition of 1,000 lb. of fortifying acid would, therefore, alter the composition by .45%.

It will be noted that the effect indicated upon the sulphuric acid is a minus quantity. This indicates that in the addition of fortifying acid, the sulphuric component is decreased, which we know to be the case.

Chart A is now plotted with these figures as a basis. Selecting a point near the center of a sheet of cross-section paper, and taking the origin at the top, the quantities representing the number of pounds of fortifying acid to be used are set off downward, according to some convenient scale.

Quantities indicating the desired change in composition of the preliminary mixing are set off to the right and to the left. The decreasing composition of the component will be taken as indicated by the direction to the left, while increasing composition is indicated by the direction to the right. A point set off upon the 1,000-lb. line and to the left, according to a change equal to .27% (calculated above) is connected by a straight line with the origin. A point upon the 1,000-lb. line to the right, equivalent to a change of .45%, is also connected with the origin by a straight line. The right-hand



line now indicates for all positions the relative alteration of the nitric acid in the preliminary mixing for the addition of a corresponding number of pounds of fortifying acid. The left-hand line indicates the change in the composition of sulphuric acid of the preliminary mixing for a corresponding addition of fortifying acid.

Chart *B* is made in a similar manner, but is drawn upon tracing cloth. The origin in this case is taken at the bottom of the paper, and the minus quantities are plotted upward to the right, while the positive quantities are plotted upward to the left.

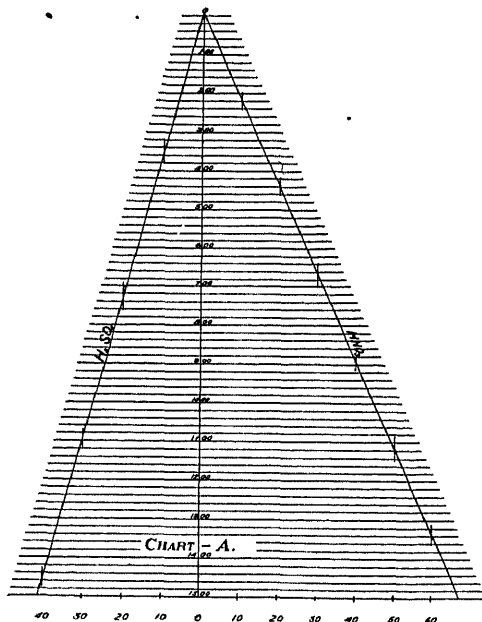


FIG. 35.—Chart A for the Redpath Graphic Method of Nitrating Acid Calculation.

Assuming the straight sulphuric to have been 97.3%  $\text{H}_2\text{SO}_4$ , by similar calculation the addition of 1,000 lb. of sulphuric acid would raise the sulphuric component .76%, while it would have lowered the nitric .52%.

By superimposing chart *B* upon chart *A*, it is possible to read by inspection the number of pounds of fortifying acid and of straight sulphuric acid which should be added in order to produce the required adjustment of the preliminary mixing.

The action of the two charts is perhaps best seen by assuming a case of the addition, for instance, of 400 lb. of fortifying acid and

200 lb. of sulphuric acid, and observing the relation between the two charts. Place the 200 lb. line of chart *B* directly over the 400 lb. line of chart *A*, and in such a position that the intersection of the left-hand diagonal with the respective pound lines coincide. It will be observed that during the addition of the 400 lb. of the fortifying acid the sulphuric acid has fallen in concentration .11%, and that from the addition of 200 lb. of sulphuric the sulphuric component is raised .15%. The algebraic sum of these two quantities, an increase of .04, will be found to be indicated by the position of the origin on chart *B*, its position now lying .04 to the right of the neutral line of chart *A*. Simultaneously, it will be found that during the

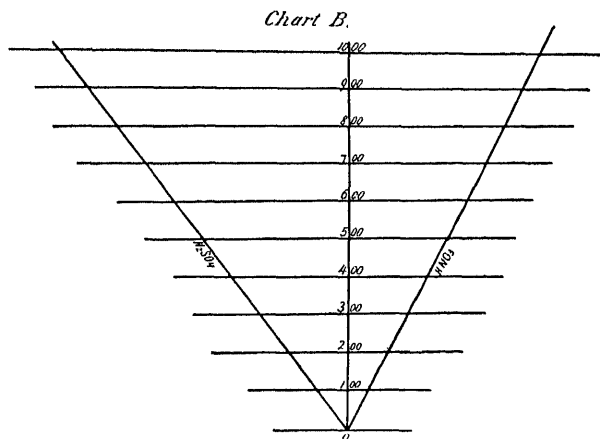


FIG. 36.—Chart *B* for the Redpath Graphic Method of Nitrating Acid Calculation.

addition of 400 lb. of fortifying acid, the nitric component was raised .18%, but that during the addition of the 200 lb. of sulphuric this component diminished .11%, a net decrease of .07%. This position on *A* will be found at a distance of .03 to the right of the position of the origin of chart *B* as it is now situated. It will also be found that there is the same distance of .03 at the level of the 200 lb. line on chart *B* between the right-hand diagonals on charts *A* and *B*. Had the diagonal on chart *B* been continued from the intersections of the diagonal on *A* with its 400 lb. line, and had it been continued downward with its own "slope" from this point, the line thus assumed, parallel to the diagonal on *B*, would have intercepted the base line at a position .03 to the left of the origin on *B* or .07 to the right of the neutral line of *A*; .07 being the algebraic sum of the alteration caused in the  $\text{HNO}_3$  component by the addition of 400 lb. of fortifying and

200 lb. of sulphuric, while the .03 is the algebraic difference between the resultant effect upon the sulphuric and nitric and components by the additions so made.

This example which we have just considered is, of course, the reverse of the usual operation. Ordinarily, from the analysis of the preliminary mixing, the required change which must be made is determined. The usual operation would then have been performed by placing the neutral line on *B* directly over that ordinate which shall represent the desired increase in the sulphuric acid component. With chart *B* in this position, raise it and lower it perpendicularly across the surface of the chart until it shall so occur that at the level of the intersection of the two left-hand diagonals there shall be a distance between the two right-hand diagonals equal to the algebraic difference of the change desired in the two components. Thus, if it were desired to raise the sulphuric acid .04, and to raise the nitric acid .07, the algebraic difference between these two quantities would be .03, and the chart *B* should be so placed that with the neutral line of *B* over +.04 on *A* there shall be a distance equal to .03 between the two right-hand diagonals at the altitude of the intersection of the left diagonals.

When such a position has been found, the quantities of fortifying acid and of sulphuric acid required will be read by inspection upon charts *A* and *B* at this same altitude.

The process of adjusting the chart *B* to its correct position will probably require about one minute, if the chart is thoroughly understood, and it will be found convenient to make use of a pair of dividers in setting off the distances required between the diagonals. It will also be found convenient to place chart *A* upon a drawing board and to insert chart *B* in a light frame, and to arrange some suitable guide for directing the perpendicular motion of this latter chart, then when the correct lateral position has been determined, clamp the guide, and maintaining this position, it is a simple matter to raise or lower the frame until the correct position is discovered.

It may be added that while the scope of this graphical method is somewhat limited by the size of the charts, it is a simple matter to reduce these quantities to a mathematical formula; so simple that the result can be obtained almost mentally in a moment. This formula will enable mixings to be made up directly from known spent if this is desired, except for the fact that variation of the composition of the fortifying would introduce greater error.

**Dangers in Connection with the Nitration of Cellulose.** With the exception of the nitration process and the possible drying of the

nitrocotton instead of solvent displacement by centrifuge or hydraulic press, the entire process is worked with a large excess of water, and the probability of explosion thus reduced to the minimum. Among the more important precautions which should be observed may be mentioned: the careful extraction of the resinous and waxy matters from the cotton previous to nitration, or their thorough elimination in the boiling and poaching processes. In the actual nitration process, the danger, except from acid burns, does not commence until the operation of wringing out in the centrifugals, and also in plunging the acid-extracted cotton into the first wash water. Great care is necessary that the wrung-out nitrocotton at once comes in contact with a large volume of water, and that it is thoroughly disintegrated so that the cold water entirely permeates the mass. If decomposition once starts, it is difficult to stop before loss of product results. The warmer the nitrated mass and the less the volume of water, the more liable is it to decompose; hence on warm and damp days the centrifugals are more apt to fire.

The patented process of neutralization with ammonia is a source of danger, as the ammonia possibly forms ammonium nitrate with traces of free acid on the fiber, and this may explode with great violence at temperatures below 40°. The increasing practice of displacement of water by propyl and ethyl alcohols, the latter made possible by the use of denatured alcohol, has almost entirely done away with the practice of drying the nitrocotton, and thus removed a great source of danger, even when the temperature of the dry-house was kept down within supposedly safe limits.

## CHAPTER IV

### SOLVENTS AND NONSOLVENTS

FOR several years after the discovery of the cellulose nitrates investigators confined their efforts in this field entirely to the perfection of this product in a dry form, and it was not until after the introduction of collodion in medicine by Maynard in 1848, and its use in photography by Scott Archer in 1851, that the possibilities of solutions of the cellulose nitrates became apparent. The "ether glue" or collodion of Maynard "puckered" and his "sticking plaster peeled;" Scott Archer could not produce films without great wrinkling and distortion; Parkes and Spill found in attempting to develop their plastic arts that it was impossible to obtain satisfactory results, being hampered and limited by too few and too hygroscopic solvents. Then, as now, the pyroxylin arts only expanded at those periods when someone added to the list of solvents or devised improved ways of combining them. In general, therefore, it can be safely said that the main factor in the development of the industrial uses of the cellulose nitrates has been due mainly to discoveries and extensions of solvents. While mechanics enters largely into modern plastics and artificial filaments, in a final analysis its success is due primarily to appropriate solvents. Camphor in the hands of Hyatt developed celluloid. Amyl acetate in the hands of Stevens laid the foundation for modern pyroxylin lacquers and imitation leathers. It was acetylene tetrachloride that enabled Lederer to produce an unflammable plastic from cellulose acetate. Nowhere when investigators attempted to expand the art were they able to attain the desired results on account of unsuitability of solvents. At the present time the world-wide endeavor to produce satisfactory non-inflammable continuous photographic films has resolved itself into a search for suitable solvents. The desirable commercial properties of pyroxylin compounds are to be obtained mainly by an adjustment of simple or compound solvents, and the superiority of the product of one manufacturer over that of another is primarily the result of the application of the knowledge and ability to manipulate solvents. A study of the historical development of the various arts comprised in these

pages will show that the failures of scientists who contributed to that progress, as viewed in the perspective of present knowledge, has been due mainly to a lack of appreciation of the fundamental importance attached to the solvent as distinguished from the pyroxylin—so many investigators erroneously regarded the cellulose nitrate as the essential factor, and the dissolving liquids or converting solids of minor importance. For this reason, the solvents of the cellulose nitrates are treated somewhat in detail; historically, because as new fields of usefulness develop, it is found that formerly discarded solvents give the properties desired, and hence a liquid abandoned as inappropriate for existing uses to-day may become of immense value in the future as the uses of the pyroxylin are industrially extended; from a manufacturing point, as satisfactory and accurate methods for the preparation of amyl alcohol and acetate are difficult to obtain, if indeed they are to be found in the usual repositories of science.

A. Parkes early found, in attempting to evaporate alcohol-ether solutions to dryness, that the film became opaque and crumbled. This he finally attributed (and truly) to water in the alcohol used, hence his process of "rendering wood spirit free from water by distillation with calcium chloride"<sup>1</sup> or "chloride of lime."<sup>2</sup> The question of moisture was not overcome in this manner entirely, for even working with anhydrous solvents, the speed of evaporation was so great that the temperature of the atmosphere in the immediate neighborhood of the film was reduced below the dew point, and so much moisture was absorbed in evaporating to dryness as to still make a white and worthless film. Parkes recognized the principle that a heavy, high-boiling but volatile solvent was necessary, and nitrobenzene<sup>3</sup> was patented. This, however, was too slow in evaporating, was poisonous, and imparted a pronounced and objectionable odor.<sup>4</sup> Aniline was found to be too weak in dissolving power, and acetic acid attacked the vessels in which the materials were manipulated and affected the eyes of the workmen. He found, however,<sup>5</sup> that by combining camphor either with sulphurous acid, turpentine or wood alcohol excellent latent solvents result, and in this respect was the pioneer in recognizing the value of camphor as an ingredient of pyroxylin mixtures.

1. E.P. 2359, 1855.

2. E.P. 1123, 1856; he distilled the wood spirit with 1-2 parts chloride of lime or  $\frac{1}{2}$  part of sulphuric acid.

3. E.P. 1313, 1865; he took 100 parts pyroxylin and added wood naphtha "distilled off chloride of calcium" and then added 10-50 parts nitrobenzol.

4. See A. Parkes, E.P. 3163, 1865; 2709, 1866.

5. E.P. 2675, 1864. Acetone was known to be an excellent solvent prior to 1864 (W. Field, J.A.C.S. 1894, 16, 544).

Daniel Spill, a co-worker with Parkes, discovered that an ethyl alcohol solution of camphor, camphor oil, or acetaldehyde<sup>1</sup> made excellent solvents.<sup>2</sup> D. H. L. Hallium formed "etherized oil" by distilling various essential oils with alcohol or ether and sulphuric acid, intended as latent solvents. C. S. Lockwood<sup>3</sup> endeavored to increase the efficiency of camphor as a latent solvent by adding a small amount of chloral or chloral hydrate to lower its fusing point. According to W. McCaine<sup>4</sup> the essential oils of cassia and cinnamon combined with alcohol or in conjunction with hydrocarbons in the proportion of 1 part to 8 of alcohol, produce a latent solvent with a wide range of usefulness. Parkes later<sup>5</sup> brought out the fact that if camphor is combined with either carbon tetrachloride, carbon bisulphide or sulphurous acid, there results a latent solvent of higher dissolving power than where camphor is used alone.

On December 19, 1882, John H. Stevens obtained six United States patents for the following direct and latent solvents, in which were summarized nearly all of the previously proposed bodies which experiment had proven would gelatinize or dissolve the various cellulose nitrates. Patent 269340 comprised oil of spearmint, nitrate of methyl,<sup>6</sup> butyric

1. E.P. 3651, 3984, 1868; 1603, 2510, 3102, 1869; U.S.P. 91377, 97454, 1869; 101175, 1870 (most important). In E.P. 1739, 1875, Spill clearly recognizes the value of hydrocarbons (by which he had in mind benzene), and was the first to point out that a pyroxylin which will not dissolve in alcohol may be made to do so by the action of benzene. It is a combined solution and gelatinization in which the benzene acts as an "exhilarative solvent." In this connection it may be mentioned that a pyroxylin which is insoluble in ethyl alcohol may sometimes be induced to go into solution by the addition of a small amount of castor oil, the latter alone having no solvent effect. Methyl alcohol with castor oil is not as efficient in this respect. Spill's favorite formula was alcohol 250, ether 150, nitrobenzol, 10, camphor 33, and benzol 250 (all parts by weight), and with aldehyde: xyloidine 27, castor oil 27, camphor 6, solvents (containing 30-50% acetaldehyde) 40 parts.

2. Spill, an assistant to Parkes, took up the work at the point where the latter failed, and achieved success. It is significant in this connection that Spill used solvents of lower volatility, less hygroscopicity and greater solvent power than did his former employer.

3. U.S.P. 246891, 1881; chloral hydrate and camphor, both solids, form a liquid when brought together. And Lockwood found that the latent solvent point of camphor could by this means be lowered in the presence of 5-20% chloral.

4. U.S.P. 262077, 1882; the advantages in the use of this oil are (1) a portion of the oil always remains in the compound to act as solvent of the solidified colloid if again exposed to heat; (2) the solvent powers are sufficiently developed to dissolve the pyroxylin at so low a temperature that sufficient heat may be obtained by the use of hot water.

5. Henry (not Alexander) Parkes, U.S.P. 265837, 1882; E.P. 1865, 1866, 1879; F.P. 132495, 1879; Belg. P. 56230, 1881; as direct solvents are introduced camphor and carbon tetrachloride; camphor and carbon bisulphide; turpentine, sulphurous acid, benzine or gasoline, but always in conjunction with camphor. Shellac is also specified as a pyroxylin solvent in connection with camphor. See also, H. Parkes, E.P. 974, 1861.

6. Methyl nitrate,  $\text{CH}_3\text{NO}_3$ , a liquid of ethereal odor resembling somewhat that of nitrous ether, boils at  $66^\circ$ , and has a sp gr. of 1.2167 at  $15^\circ/15^\circ$ . At one time it was used considerably in the manufacture of certain organic dyestuffs (iodine green and iodine violet) but owing to a series of fatal explosions which followed

ether, valeric ether,<sup>1</sup> benzoic ether,<sup>2</sup> formic ether,<sup>3</sup> salicylate of methyl,<sup>4</sup> formate of amyl,<sup>5</sup> acetate of amyl, butyrate of amyl,<sup>6</sup> valer-

its employment, its high volatility and expense of production, it is no longer used. It explodes when struck or when its vapor is heated, and is an excellent solvent of resins and the cellulose nitrates.

1. Ethyl *isovalerate*,  $C_5H_5 \cdot C_5H_9O_2$ , a colorless, mobile oil, readily soluble in alcohol, ether and chloroform, boils at 134-135°, and has a sp.gr. of 0.8714, at 15°/15°. Its ethyl alcohol solution finds extensive use as an ingredient in artificial fruit essences, principally those of strawberry and raspberry. It is 6 or 8 times more expensive than amyl acetate, and has never been used as a direct solvent on account of the cost of production. The bouquet developed in crude fusel oil which has been partially oxidized into valeric acid with potassium bichromate and then converted into acetate contains small amounts of ethyl as well as amyl valerate.

2. Ethyl benzoate,  $C_2H_5 \cdot C_7H_5O_2$ , a colorless liquid of characteristic and aromatic smell, and having a boiling point of 213° and a sp.gr. of 1.047 at 20°/4°, may be readily prepared by the action of ethyl alcohol on benzoic acid in the presence of a strong dehydrating agent. It is an excellent solvent of copal, dammar, and sandarac as well as the cellulose nitrates, the cost of benzoic acid and relatively high boiling point being the principal drawbacks to its use in large quantities. Benzyl benzoate, a constituent of Peru and tolu balsams, is of interest, from the use of the latter two products in pyroxylin lacquers to impart toughness to the film. Propyl, butyl, and amyl benzoates, with boiling points of 229°, 247° and 261° respectively, have a too low volatility to be acceptable solvents. Methyl benzoate is too costly.

3. Ethyl formate,  $C_2H_5 \cdot CO_2$ , a thin, mobile liquid, possessing a rather pleasant penetrating smell and cooling taste, boils at 55° and has a sp.gr. of 0.9061 at 20°/4°. One part is said to dissolve in 9 parts of water at ordinary temperature. It is readily soluble in alcohol and ether, and possesses an odor of peach kernels. It is not only exceedingly hygroscopic, but decomposes in contact with moisture, liberating formic acid. This property alone would render it unfit as a solvent for lacquers, artificial leathers and photographic films, the free acid tending to induce decomposition of the pyroxylin. This is not to be confounded with ethyl orthoformate, which boils at 145-146°. The corresponding methyl formate is said (Mayberry, J.A.C.S., 1883, 5, 259) to be present in crude wood spirits, and to account in a measure for the excellent solvent properties of the latter. Commercial ethyl formate is usually contaminated with the methyl ester, due to its manufacture from crude wood spirit. Methyl and ethyl formates find use in the formation of artificial arrack and rum essences.

4. Methyl salicylate,  $(CH_3 \cdot C_7H_5O_2)$ , the principal constituent of oils of winter-green and sweet birch, is a colorless, strongly refracting liquid which boils at 221°, and has a sp.gr. of 1.197 at 0°/7°. It is made indirectly from toluene, but as yet not at a sufficiently low price which will enable it to compete with amyl acetate. This ester is an excellent solvent of pyroxylin, and is used to a very limited extent to correct objectionable odors in other solvents, principally acetone oils and wood oils. Ethyl salicylate is the equal of the methyl ester as a pyroxylin solvent. The phenyl ester, known also as salol, forms an excellent latent solvent, and is readily soluble in alcohol and fusel oil.

5. Amyl formate,  $C_5H_{11} \cdot CO_2H$ , a colorless liquid of penetrative odor, boils at 116°, and has been advocated as a desirable pyroxylin solvent. In volatility, stability and great dissolving power it appears to be the equal of the corresponding acetate, and only the high cost of formic as compared with acetic acids prevents its commercial use in large amounts. A. Bedal (E.P. 12157, 1899) has obtained protection for the manufacture of amyl formate. Both propyl and butyl formates are also stated to be excellent solvents, and have boiling points between ethyl and amyl alcohols. Ethyl formate decomposes upon long contact with moisture.

6. Methyl butyrate,  $C_5H_{11} \cdot C_4H_9O_2$ . The *isoamyl* ester boils at 176°, and has a sp.gr. of 0.8823 at 0°/4°. A mixture of methyl butyrate (b. pt. 101°) with amyl butyrate is stated to produce a solvent, which in all its physical deportment more closely resembles amyl acetate than any other simple or mixed solvent. These two, as well as propyl, *isopropyl* and butyl butyrates, which boil at 143°, 128°, and 165° and have gravities at 0° of 0.8872, 0.8787, 0.8885, are all excellent solvents of



ianate of amyl,<sup>1</sup> sebacylic ether,<sup>2</sup> oxalic ether,<sup>3</sup> amylic ether,<sup>4</sup> amylic oxide,<sup>5</sup> oxidized wood alcohol,<sup>6</sup> oil of cassia,<sup>7</sup> oil of cherry laurel,<sup>8</sup> heavy cinnamon oil,<sup>9</sup> oil of melissa,<sup>10</sup> rectified oil of birch tar,<sup>11</sup> and oil of pennyroyal.<sup>12</sup> Patent 269341 included as latent solvents oils of car-

pyroxylin, besides dissolving many resins including copal, sandarac, mastic and elemi, and in addition to this are practically insoluble in water, so that they may be obtained in an anhydrous state without difficulty. The only obstacle to their extensive use is the cost of butyric acid or butyrates to produce them. They are all colorless, mobile liquids, with characteristic odors.

1. Amyl valerianate,  $C_5H_{11} \cdot C_6H_{11}O_2$ , boils at  $188^\circ$  (Kopp and R. Schiff, Ann., 1886, 234, 344) and has a sp.gr. of 0.87 at  $0^\circ/20^\circ$ . It smells like apples when dissolved in 7 parts alcohol. It is used principally in artificial flavors, being too slow in evaporation to make a desirable pyroxylin solvent, although it dissolves the latter with avidity. The methyl, *n*-propyl, and isobutyl valerates, which boil at  $116^\circ$ ,  $156^\circ$ , and  $169^\circ$ , would be more satisfactory. Butyl valerate is said to dissolve the harder copals and ambers without a preliminary heating of the latter, at the same time dissolving a wide range of nitrocelluloses. The valerianates are several times more costly than the corresponding acetates.

2. Commercial sebacic ether is a mixture of methyl-, monoethyl- and diethyl-sebacates, all of which have high boiling-points (above  $250^\circ$ ). Sebacic acid results from the dry distillation of fats under partial vacuum, and the sebacates are made by treatment of the acid with the desired alcohol and a dehydrating agent. Although energetic solvents, they are not used on account of their cost. A number of wine, brandy and bitters flavors contains this ester in small amounts as a "fixative," to render the other odors more permanent and distinctive.

3. Principally diethyl oxalate, with small amounts of monoethyl oxalate (ethyl oxalic acid). This ester is usually prepared by heating ethyl alcohol with oxalic acid. A portion of the oxalic acid is reduced to formic acid, so that the commercial ester usually contains ethyl formate as well. It is a colorless oil with slight odor, decomposed by water and easily soluble in alcohol.

4. 5. Amyl ether or amyl oxide,  $C_{10}H_{22}O$ , exists in two forms, *iso*amyl oxide,  $(C_5H_{11})_2O$ , and *iso-sec*-amyl oxide. The former boils at  $173^\circ$ , and the latter at  $163^\circ$ . Both are formed upon treating crude fusel oil with a dehydrating agent (sulphuric acid) and distilling. They are ethers, not esters. Formerly several patents were obtained for the production of these simple and mixed ethers by the distillation of fusel or other alcohols alone with sulphuric acid or mixed alcohols, as methyl, ethyl, propyl and amyl alcohols with the same acid. It was found that their high boiling point and difficulty in obtaining in a neutral state were serious drawbacks to their extended commercial use.

6. A number of imperfectly characterized bodies results, including probably methylal.

7. The solvent power of this essential oil rests entirely upon the cinnamic aldehyde present. A good grade of cassia oil should assay 80-85% cinnamic aldehyde by means of the Hanus (Z.U.N.G., 1903, 6, 817) gravimetric semioxamazone (J. pr. Chem., 1874, 10, 196) method. (See Schimmel's Semiannual Report, 1904, 19.) Pure cinnamic aldehyde, produced synthetically is an excellent deodorizer in collodions and pharmaceutical preparations containing pyroxylin in solution.

8. The latent solvents present in this oil are considered to be pinene, cineol and geraniol. (It is geraniol and citronellal which give to oil of citronella its latent power as a cellulose nitrate solvent.)

9. This consists of not clearly defined sesquiterpenes and cinnamic aldehyde, with small amounts of benzyl benzoate. (The value of balsams tolu and Peru as solvents rests mainly upon the presence of benzyl benzoate, and less so upon the benzyl alcohol, and benzyl cinnamate normally present.)

10. Oil of balm.

11. A series of experiments made by the author, with a sample obtained from Schimmel & Co., were entirely negative as a solvent, the oil not even gelatinizing the pyroxylin.

12. Consists principally of pulegone as the solvent constituent.

away,<sup>1</sup> hyssop,<sup>2</sup> sage,<sup>3</sup> tansy,<sup>4</sup> cloves,<sup>5</sup> or wintergreen and mixtures of them. In patent 269342 there are embraced dinitrobenzene<sup>6</sup> and coumarin.<sup>7</sup> Number 269343 designated acetone, acetate of ethyl, acetate of methyl, fusel oil, amylic alcohol, oils of chamomile,<sup>8</sup> fennel seed,<sup>9</sup> palmarosa,<sup>10</sup> and worm seed, but always in conjunction with camphor. No. 269344 included oils of hyssop, sage, tansy, wormwood fennel seed, cloves, cinnamon, anise, sassafras, chamomile, wintergreen, caraway or dill, but in combination with fusel oil, acetal,<sup>11</sup> <sup>12</sup> nitrate of amyl,<sup>13</sup> or mixtures of any of them. In the last patent—269345—Stevens enumerated ethyl or methyl alcohol with nitrate of amyl, nitrite of amyl,<sup>14</sup> oils of chamomile, valerian, golden rod, sassafras, cinnamon, cunin, cynae ether, dill, elecampane, fennel seed, heavy wine,<sup>15</sup> wormseed, myrtle, laurel, marjorem, peppermint,

1. Contains a terpene,  $C_{10}H_{16}$ , identical with citrene and carvol.

2. See Schimmel's Semiannual Report, 1906, 41.

3. The solvent power is said to be due to salviol, the latter increasing with the age of the oil; hence old and partially resinified oils of sage are more energetic solvents than when freshly distilled.

4. According to Beuylants (J. Ph., 1877, (4), 26, 393; Ber., 1878, 11, 449; Persoz, C.R., 1839, 8, 433) the cellulose nitrate solvent constituent is tanacetyl hydride, which is present to the extent of about 70%.

5. The latent solvent is eugenol and *isoeugenol*, caryophyllene being a strict non-solvent. Therefore the solvent value of this oil is in direct proportion to the amount of eugenol present.

6. Exists in three (*o*-, *m*-, and *p*-) modifications. The commercial product consists mainly of meta-dinitrobenzene, colorless needles, melting at 90°, and readily soluble in boiling alcohol. The trinitrobenzenes, of which the symmetrical derivative is the most important, have also been patented as latent solvents, and on account of higher boiling point, are less volatile and possess a less pronounced odor than the di- or mono-nitrobenzenes.

7. The odoriferous principle of the tonka bean, and used in combination with vanillin, for "compound" extracts of vanilla. The cost of coumarin has never caused it to be used. The same may be said of vanillin, heliotropin, menthol, thymol, . . . similar bodies.

8. *Tl* . . . . . *utyl isobutyrate*, *isobutyl angelate*, *amyl angelate*, *amyl tiglate*, *hexyl angelate*, *hexyl tiglate*, and *anthemol*. (Fittig and Kobig, Ann., 1879, 195, 106; van Romburgh, Rec. Trav. Chim., 1886, 5, 220; Demarçay, C.R., 1873, 77, 360), all of which, with the possible exception of the last-named constituent, are direct active solvents.

9. Solvent effect due to anethol and phellandrene (Cahours, Ann., 1812, 41, 75).

10. At present very expensive.

11. A peculiar, agreeable-smelling colorless liquid, difficultly soluble in water, readily in alcohol and ether. Present in crude spirit, and in imperfectly oxidized alcohol. Acetal is said to be an energetic, direct solvent with the proper boiling-point (104°) for satisfactory volatilization, the cost of production only precluding its extended use.

12. The apparently abnormally high solvent action of certain wood spirits have been traced to large amounts of acetal contained therein.

13. This explosive liquid has been exploited as an efficient solvent for refractory amber and copals. E. Liebert (D.R.P. 51022, 1889) proposes to add it to nitroglycerol to decrease its sensitiveness to shock.

14. A yellowish liquid smelling like nitrous ether; becomes acid on exposure to air.

15. Light oil of wine is obtained in the preparation of ether by distilling alcohol with sulphuric acid. (For composition see Hartwig, J. pr. C., 1881, (2), 23, 449). Heavy oil of wine, which passes over when the temperature is raised above the

rue, cinnamon, palmarosa, rosemary or erigeron. In patent 269340,<sup>1</sup> by mentioning amyl acetate, Stevens laid the foundation upon which the modern pyroxylin industry has arisen. It was found that the essential oils, while excellent solvents, were too costly for general use, and with the exception of a few, have never passed beyond the experimental stage.

J. Jarvis<sup>2</sup> in extending the latent solvents found dammar, guaiac and mastic useful in the proportion of pyroxylin 100, gum resin 40, with alcohol (wood or grain) 50 parts, adding a small amount of camphor to decrease brittleness, if desired. In conjunction with camphor, O. Amend<sup>3</sup> has obtained protection for the use of amyl chloracetates as a direct solvent,<sup>4</sup> while the next year A. Orr<sup>5</sup> was granted a patent for a liquid which he calls "chloracetate of chloramyl," which appears to be a physical mixture of amyl acetate and chloride.

C. R. Schüpphaus, in behalf of the American Zylonite Company of New York, was granted in 1889 a series of United States Patents embracing latent cellulose nitrate solvents, and comprising<sup>6</sup> propyl and isobutyl alcohols,<sup>7</sup> anthraquinone in alcohol,<sup>8</sup> isovaleric aldehyde or its derivatives,<sup>9</sup> amyliidendimethyl- and amyliidendiethyl-ether,<sup>10</sup>

boiling point of ether, consists of ethyl sulphate, mixed with olefines (Clacsson, J. pr. C., 1880, (2) 19, 259; Serullas, Ann. Chim. Phys., 1828, (2), 39, 152). Both are excellent pyroxylin solvents, but too costly for commercial use.

1. A disclaimer filed Feb. 18, 1896, to U.S.P. 269340, disclaims photographic sensitized solutions, pyroxylin compounds or solutions used pharmaceutically or for surgical purposes, oil of spearmint, methyl nitrate, methyl salicylate, amylic ether, and oils of melissa, birch tar and pennyroyal. Recites E.P. 2350, 1855; 2675, 1864; 3651, 1868; 1603, 2510, 3102, 1869; U.S.P. 105338, 156358. Disclaimer to U.S.P. 269344, filed same day, includes, "any pyroxylin compound other than those used for photographic purposes as distinguished from such pyroxylin compounds as . . . solutions and pyroxylin solutions used for pharmaceutical and surgical purposes." Disclaims use of fusel oil in pyroxylin combinations which are not used for manufacturing purposes, and fusel oil in conjunction with oils of hyssop, tansy, wormseed, cinnamon (light), sassafras, and chamomile; acetal and amyl nitrite and nitrate.

2. U.S.P. 329313, 1885.

3. U.S.P. 371021, 1887; reissue 10879, 1887; chloracetates of amyl include the three chlorine substituted acetic acid esters, i.e., amyl monochloracetate, dichloracetate and trichloracetate. The amyl chloracetates boil at much higher temperatures than amyl acetate.

4. U.S.P. 372100, 1887, O. Amend, comprises amyl chloral, monochlorvaleraldehyde, dichlorvaleraldehyde and amyl chloride. Of the eight known isomeric amyl chlorides, the isochloride boiling at 90.5° is the best known and most readily prepared. It is a feeble direct solvent.

5. E.P. 487, 1888; abst. J.S.C.I., 1889, 8, 204.

6. U.S.P. 410204, 1889.

8. U.S.P. 410206, 1889.

7. U.S.P. 410205, 1889.

9. Isovaleric aldehyde (valeral), formed by the oxidation of amyl alcohol, is a neutral oil, with pungent fruity odor, readily polymerizes on keeping, and mixes with alcohol and ether. It boils at 92.5°, and is difficultly soluble in water. Valeral, like acetaldehyde, and the other lower members, does not dissolve the cellulose nitrates directly, but only when in a "mixed solvent."

10. Isoamyliideneacetoacetic ether, and isoamyliidene-*m*-amidobenzoic acid are both stated to be direct solvents.

$\alpha$ - or  $\beta$ -naphthol in alcoholic solution<sup>1</sup> glycerol acetate,<sup>2</sup> especially as a base for a pyroxylin plastic printing ink,<sup>3</sup> and palmatin<sup>4</sup> and stearone<sup>5</sup> in alcoholic solution.

As resin lacquer solvents, Lamb and Boyd in 1889 patented the use of combinations of fusel oil and benzene, decreasing the amount of fusel oil to increase the speed of evaporation of the lacquer. The late August Scher followed three years later<sup>6</sup> with a series of ketones as direct solvents, and which included propion,<sup>7</sup> butyron,<sup>8</sup> capron,<sup>9</sup> methylethyl ketone, methylpropyl ketone, methylbutyl ketone,

1. U.S.P. 410207, 1889.

2. U.S.P. 410208, 1889. Glycerol forms a mono-, di-, and tri-acetate, known respectively as monoformin, diformin and triformin. They are heavy oily liquids, resembling in physical appearance glycerol, and like the latter, dry very slowly. This property Schuppheus proposes to utilize in his process as described in the above patent, for the production of printing inks, which would have as a basis a cellulose nitrate solvent, so that the impression from the press would actually dissolve the superficial pyroxylin coat, and thus form a firm anchorage.

3. U.S.P. 410209, 1889.

4. Glycerol, being a tri-hydric alcohol, can form esters with one, two, or three monovalent acid radicals. Similarly to the three nitroglycerols, or acetoglycerols, combination with palmitic acid, resulting in the formation of mono-, di-, or tri-palmatin is possible. The latter constitutes some of the natural fats. Great pressure is required to cause pyroxylin and the palmatins to dissolve. In U.S.P. 598648, 1898, Schuppheus records discoveries made with similar bodies, and produced by introducing another acid radical into the acetins and allied substances, whereby the objectionable hygroscopic qualities are absent without serious impairment of the solvent power. When a current of HCl is passed through a mixture of equal volumes of glacial acetic acid and glycerol heated to 100°, acetodichlorhydrin (isomers) is formed, which is saponified and a dichlorhydrin results. Hence the technical product consists of both. Acetochlorhydrin is not hygroscopic and is more particularly valuable in its application in printing inks for pyroxylin surfaces. By introducing the acid radicals of benzoic, oleic and nitric acids into the acetins, it is claimed closely allied glycerol esters of distinct value, are formed. (Glycerol monobenzoate (monobenzoin), benzomonoacetin, benzodiacetin, benzochlorhydrin, monoolein (glycerol monooleate), oleoacetin, oleodiacetin, oleoacetates or acetooleates of glycerol, dinitromonoacetins and mononitrodiaacetins are combinations named which appear to be of more or less value.

5. This is a ketone of the same class as acetone. It is di-heptadecyl ketone, an oily liquid, obtained by heating stearic acid to 210°. Its solvent action is only apparent upon pressure.

6. U.S.P. 470451, 1892; J. H. Stevens (U.S.P. 595355, 1897), adds ethylpropyl, ethylpentyl, ethylhexyl, propylbutyl, propylpentyl, propylhexyl and butylpentyl ketones.

7. Diethyl ketone (metacetone) is a mobile oil lighter than water, and very soluble in alcohol and ether. It boils at 101°, smells like acetone, is an excellent pyroxylin solvent, and is present in an impure form in the commercial acetone oils in combination with methylethyl, methylpropyl and dipropyl ketones. As a general solvent, diethylketone is superior to ordinary (dimethyl) acetone.

8. Dipropyl ketone boils at 115°, and diisopropyl ketone at 121°. Both resemble acetone in general properties, being superior to the latter on account of lower volatility and less hygroscopicity. A mixture of these two ketones in equal proportions is said to produce a solvent which nearly simulates amyl acetate in physical behavior, and is superior in that it is a much more energetic solvent of resins and essential and fixed oils. Also valerone (dibutyl ketone).

9. Di-*n*-amyl ketone, boiling at 226° and prepared by distilling, calcium caproate, is said to be the principal constituent in commercial heavy acetone oil (which see). It is a solid, melting at 15°, but readily soluble in other ketones.

methylamyl ketone, methyl valeral<sup>1</sup> and ethylbutyl ketone. These bodies are contained in the various fractions of commercial "light" and "heavy" "acetone oils," and are excellent solvents of both pyroxylin and resins.<sup>2</sup> The next year Leonard Paget<sup>3</sup> registered five U.S. patents in which he claims the discovery that mixed ethers obtained by the etherification of methyl, ethyl, propyl, butyl and amyl alcohols in the presence of a dehydrating agent as sulphuric acid, result in the formation of direct and indirect solvents of distinct value. Direct solvents are claimed to result when ethyl alcohol in excess is combined with fusel oil, and indirect solvents with butyl and amyl

1. Methylacetone (methyl ethyl ketone) resembles acetone very closely. It is an agreeable-smelling liquid, boiling at 81° (same temperature as ethyl alcohol). It is superior to acetone as a solvent in every respect, possessing all the desirable properties of the latter, and in addition is less volatile and hygroscopic. A mixture of methylacetone and ethyl alcohol forms a solvent boiling at the same temperature, and much superior to the ether-alcohol combination, the methylacetone allowing of greater attenuation than ether without destroying the solvent effect due to the increasing increment of alcohol. Methylpropyl ketone (ethylacetone), boiling at 102°, is a liquid but slightly soluble in water, methylisopropyl ketone, (dimethyl *l*-acetone, amylene oxide), a liquid boiling at 94°; methylbutyl ketone, and other mixed ketones, are constituents of commercial "acetone oils."

2. In the usual process of manufacture of acetone (U.S.P. 385777, 393079, 1888; 535552, 1895; 608019, 1898; 648389, 1900; 835501, 1906; E.P. 2816, 1898; 25994, 1901; 9936, 1902) the pyroligneous acid consisting of acetic and higher homologous acids is neutralized with milk of lime, the calcium salt dried and subjected to destructive distillation, ketones resulting. When the distillate reaches the neighborhood of 62° (acetone boiling at 56.5°) the receiver is changed, the fraction from that temperature up to about 125° being retained separately as "light acetone oil," and above 125° as "heavy acetone oil." But little has been done in the use of the heavy oil as a pyroxylin solvent on account of difficulty in purification, characteristic pungent odor and low volatility. The lighter oil is a valuable solvent and finds ready market in the lacquer and imitation-leather industries. It is necessary to further purify it before use and this is done by first distilling with a small amount of ferric, cupric, stannous, manganous, nickelous or cobaltous chloride (not calcium or magnesium chlorides), after which is given a final distillation with sodium thiosulphate, phosphoric acid, acidified oxalic acid, barium peroxide or perborate. Thus prepared it is a colorless limpid liquid, not hygroscopic, difficultly miscible with water, miscible with alcohol, chloroform, ether, fusel oil and amyl acetate, and an excellent solvent for pyroxylin and resins. The "heavy acetone oil" should prove a useful ingredient in solvent paint removers on account of its low volatility and deep penetration. (For full descriptions, manufacture, etc., see P. Baechland, *Rev. Chim., Ind.*, **15**, 133, 240; G. Michaelis and W. Mayer, E.P. 8523, 1885; F. Crane, E.P. 6543, 1892; J.S.C.I., 1898, **17**, 266, 485; 1899, **18**, 292, 405; 1902, **21**, 164, 1271).

3. U.S.P. 494790, 494791, 494792, 494793, 507749, 1893; a mixture of sulphuric acid 25, fusel oil 25, wood alcohol 15, grain alcohol 10 (all parts by weight) are distilled together and the distillate redistilled with 15% of its volume of glacial acetic acid. Or to prepare acceptable mixed ethers, for 25 parts conc. sulphuric acid take (a) ethyl alcohol 15, methyl alcohol 10, fusel oil 50; or (b) methyl alcohol 25, fusel oil 50 (all parts by weight). The solvency of the latter combination is greater than the former, whereas, as is well known, a mixture of the above named alcohols in the quantities stated would exert little, if any, dissolving effect on pyroxylin. These simple and mixed ethers were found difficult to obtain neutral, and offered but little advantages over amyl alcohol and ether in simple mixture. Moreover if the etherification was not very carefully conducted the same ethers were not always produced in equal amounts, and the solvents resulting lacked in uniformity of action.

alcohols.<sup>1</sup> J. Perl<sup>2</sup> extended this idea of chemical combination of two or more simple solvents, and evolved ethyl aceto-acetate (aceto-acetic ester) to dissolve pyroxylin directly, methylated ether<sup>3</sup> being claimed to possess similar properties. C. Borgmeyer extended the list of active solvents and combinations containing them, by the introduction of certain essential oils as oil of lemongrass,<sup>4</sup> oils of cedar leaf, bitter almonds, rue, pimento,<sup>5</sup> synthetic oil of cassia (cinnamic aldehyde),<sup>6</sup> Chinese cinnamon, hemlock, wormwood, caraway chaff, savin, cajeput, spruce,<sup>7</sup> sandalwood, cubebs, ginger, bay, clove buds and citronella,<sup>8</sup> synthetic oils of sassafras, red thyme, tansy and peppermint,<sup>9</sup> or a combination of ozonized oils with chloracetates.<sup>10</sup>

G. Zeller in 1894 described a series of indefinite bodies<sup>11</sup> obtained by subjecting an alcohol to the action of an oxidizing agent in the presence of a compound organic acid, combining the aldehyde and acid radical to a series of "aldesters," benzene<sup>12</sup> and hydrochloric

1. In U.S.P. 507749, improvement in the solvent power of weak solvents is claimed by the addition of an ozonizing process by ozone prepared by the electrolysis of air, the ozone being freed from moisture before use. The solvent action of oil of camphor becomes greatly increased, it is claimed, by being sprayed into a chamber containing ozone; oil of turpentine, practically a nonsolvent of pyroxylin, treated with ozone to saturation, becomes an active solvent; oil of caraway seed, which is practically non-drying, although a good pyroxylin solvent, becomes possessed of drying properties upon being ozonized; improvement in solvent power of methyl alcohol, acetone, acetal, ethylamyl ether, fusel oil and camphene is claimed to result when acted upon by ozone.

2. F.P. 233727, 1893, abst. J.S.C.I., 1896, 15, 729.

3. A physical mixture of methyl alcohol and ethyl (ordinary) ether.

4. U.S.P. 502546, 1893; known scientifically as *Oleum andropogani citrati*, is a powerful, active solvent of pyroxylin, yielding clear, thin solutions, the drawbacks being slowness of evaporation and cost.

5. U.S.P. 502547, 1893; oil of cedar leaf, being the cheaper, would be preferable.

6. U.S.P. 502921, 1893; an excellent solvent, but of powerful odor and too costly.

7. U.S.P. 503401, 1893; they are not active solvents individually, but only when in combination with ethyl alcohol; oil of caraway chaff is much less expensive than oil of caraway seed (U.S.P. 269341). The alcoholic solutions are all miscible with each other.

8. U.S.P. 503402, 1893; the solvent action of the above named six essential oils is retarded by the addition of fusel oil to any one of them, while oils of ginger, bay, clove buds and citronella with grain alcohol are active solvents, oil of sandalwood or cubebs with ethyl alcohol has no dissolving effect. Oil of cloves (U.S.P. 269340) separates out from many pyroxylin solutions, while oil of clove buds does not do so, and requires no heat to develop its active solvent power.

9. U.S.P. 504905, 1893; artificial sassafras oil consists mainly of safrol; artificial oil of red thyme of thymol; artificial oil of peppermint by distillation together of *Mentha pulegium* (European pennyroyal) and *Mentha crispata* (common curved leaf mint) with lemon peel.

10. U.S.P. 507964, 1893, C. Borgmeyer and L. Paget; to form a lacquer drying evenly at atmospheric temperatures the inventors take amyl acetoacetate 20, ozonized fusel oil 5, wood alcohol 5, benzene 15 (all gal.), and dissolve therein 20 lb. pyroxylin. The amyl acetoacetate may be substituted by one-half amyl acetate, the former combination being preferable.

11. U.S.P. 518386, 518387, 518388, 1894; 555596, 1896.

12. A method of preparation of these bodies would be to take amyl alcohol 4, butyl alcohol 2, acetic and formic acids each 1, and subject this mixture to the

acid <sup>1</sup> being added before distillation. While solvents may be produced in this manner, their composition is so varied that it is difficult to obtain dependable results by their use, and are not employed at the present day. Emile Bronnert, in 1896, experimenting along lines of artificial silk production, obtained satisfactory results with certain nitroderivatives, and patented <sup>2</sup> methylated spirits, nitroglycerol, nitrobenzene, binitrobenzene in alcoholic, ethereal or chloroformic solutions, and nitronaphthalin <sup>3</sup> and benzanilid, <sup>4</sup> priority of discovery of the latent solvent action of the latter two being claimed. Bronnert appears to be the first to endeavor to decrease the well-known inflammability of the usual solvent combinations, using for this purpose an ethyl alcoholic solution of calcium chloride, this combination being but slightly inflammable, not liable to spontaneous combustion or explosion on concussion, and at the same time possessing active direct solvent properties. <sup>5</sup> It should be noted that the ready solubility of calcium chloride in water and its hygroscopic nature would not render a lacquer comprising this combination impervious to moisture or to the gases of the atmosphere. Although Spill described the use of acetaldehyde, R. Strehlenert extended its uses, <sup>6</sup> both alone and combined with ethyl and other alcohols, and Hellberg and Pertsch developed methyl and ethyl chlorides for the same purpose. <sup>7</sup> Upon oxidizing mixtures of the paraffin alcohols, as commercial fusel oil unrectified, with sulphuric acid and chromate, action of sulphuric acid 2 (all parts by weight), with manganese dioxide 1, separating, neutralizing and redistilling the mixed solvent formed.

1. Benzine 2, is added to above formula before esterification.

2. A mixture of 8 parts ethyl alcohol and 1 part methyl alcohol, but a term now including any combination of ethyl alcohol denatured with methyl alcohol. See U.S.P. 573132.

3. Mononitronaphthalin, a deep yellow crystalline mass, existing in several isomeric forms, is a latent solvent, either in solution, or alone with pressure. The di-, tri- and tetra-nitronaphthalins are said to possess similar latent solvent properties, but their intense yellow color, which increases with the number of nitro groups introduced, is a serious drawback to their use, especially in light-colored combinations.

4. Benzoyl aniline, a crystalline body insoluble in water, but easily soluble in ethyl alcohol, chloroform or ether. It has a melting point of 160° and its solvent action is only active in the liquid state, it is claimed.

5. Other chlorides, bromides, iodides or fluorides of calcium, magnesium, iron, tin, copper, zinc, cobalt, manganese, nickel and some other metals, are soluble in alcohol, non-inflammable, and are efficient in this respect, but like calcium chloride all are soluble in water, and hence not impervious to the atmosphere.

6. Acetaldehyde is a colorless, . . . liquid, difficultly soluble in water, more soluble in alcohol and . . . in the first portions obtained by rectifying spirit that has been filtered through charcoal, the latter oxidizing the alcohol to aldehyde. This fluid is not a direct solvent, exerting its dissolving power only in combination. The aldehydes of propionic and the higher homologous acids have no commercial importance in this connection. The polymers of acetaldehyde—paraldehyde and . . . have been used little, if at all.

7. Methyl chloride is a gas at . . . pressures, ethyl chloride boiling at 12°. The volatility of either is so great as to preclude their extended use as solvents.

bichromate or permanganate, there results a series of compounds of obscure and varying composition, which, however, are excellent direct pyroxylin solvents.<sup>1</sup> If these alcohols be distilled with a dehydrating agent and benzoic or salicylic acids,<sup>2</sup> methyl-, ethyl-, propyl-, etc., benzoates and salicylates are formed, all of which are active solvents, the lower boiling point members being direct and those of higher molecular weight indirect in their solvent action. They possess the additional advantage of a pleasant and ethereal odor, and would undoubtedly find extensive commercial use if the cost of benzoic or salicylic acids could be lowered to a point where it might favorably compete with acetic acid.

The use of liquid solvents composed of physical mixtures of simple substances has been attended with more or less difficulty, due especially to the varying volatilities, or lack of harmony or chemical incompatibility between the various constituent ingredients of the mixed solvent. This is often apparent in evaporating a thin solution to dryness, where the speed of evaporation varies due to the diversified solvent volatility, there appears considerable variation in surface appearance and homogeneity of the film. J. H. Stevens has sought to overcome this<sup>3</sup> by forming mixed esters of formic acid and adjusting the alcohols, in such proportions that a continuous definite speed of evaporation is possible. In order to approach in other solvents the valuable properties of amyl acetate—its slow volatility and immiscibility with water—this inventor has devised a series of carbonic esters,<sup>4</sup> diethyl and diamyl carbonate being preferred—and they are said to possess the advantage over amyl acetate in being

1. U.S.P. 559823, 1896, J. H. Stevens. A suitable compound may be prepared, according to the inventor, by taking crude fusel oil 2, manganese dioxide 3, sulphuric acid 3, water 2 (all parts by weight), mix, place in a still and carefully fractionate. Dehydrate over calcium chloride and neutralize. For the lower alcohols as methyl or ethyl, a limited oxidation is considered preferable, equal parts of wood, grain and amyl alcohols being distilled with manganese dioxide  $\frac{1}{2}$ , sulphuric acid  $\frac{1}{2}$  and water 1 (parts by weight). The solvents are said to be better adapted for use with amyl acetate and acetone.

2. U.S.P. 559824, 1896; J. H. Stevens combined wood spirit, grain alcohol, crude fusel oil each 4, potassium benzoate 9, sulphuric acid 6 (all parts by weight), which are mixed together and heated for about 30 minutes at 100°, water being then added, when the esters float on top. They are then removed, neutralized, dehydrated and rectified.

3. U.S.P. 561624, 1896; in which methyl and ethyl alcohol and crude fusel oil 1 part each, with potassium formate 3 parts (by weight) are distilled with sulphuric acid 2 parts. Amyl formate is a most excellent direct solvent of pyroxylin, superior in many ways to amyl acetate, two of which are less pronounced and disagreeable odor and lower boiling point, and hence quicker drying properties.

4. U.S.P. 610728, 1898; methyl carbonate is highly volatile, yet practically immiscible with water; the amyl ester is of low volatility, insoluble in water, and of but faint odor. In a pure condition they are stated to be nonsolvents, a small amount of alcohol rendering them active.



nearly odorless. G. Walker<sup>1</sup> has described a process of producing an active solvent both of pyroxylin and resins, by fractionating the tar from hard woods and rectifying the lighter portions. The liquid has a very pronounced odor so that it is used in small amounts only in pyroxylin formulas, but its dissolving property is so great that it is especially useful in combinations where the solvent power is especially low. These solvents are used commercially at the present day.

In 1903 Stevens<sup>2</sup> again added another series of mixed ethers of the paraffin series and obtainable by distilling methyl, ethyl, propyl, butyl and amyl alcohols interchangeably with a dehydrating agent as concentrated sulphuric acid, the products so formed being direct solvents.<sup>3</sup> E. Todd<sup>4</sup> has added to the possible number of useful solvents, and attempted to increase the volume without a corresponding decrease in activity of a given solvent, as amyl acetate, by adding benzine to the fusel oil before acetation, whereby the yield of finished product is increased, and according to the patentee, without serious impairment of the solvent action.<sup>5</sup> Schüpphaus adds<sup>6</sup> methyliso-

1. U.S.P. 604181, 1898; by the term "hard woods" is understood the woods of the leaf-trees—beech, birch, maple, and oak, for example—as distinguished from the needle-trees, such as pine. When the tar of these woods is distilled in a suitable apparatus until one-half of its weight of the tar has been distilled at a temperature of 100° to 250°, the first half of the distillate will consist of pyro-ligneous acid containing methyl alcohol and an oil lighter than water, together with some oil heavier than water which has been carried over mechanically with the aqueous vapor. This mixture of light oil and pyro-ligneous acid is separated by settlement and decantation and the acid and a certain portion of creosote which it contains are completely removed from the separated light oil by agitation with caustic alkali, after which the oil is resubmitted to distillation at a temperature ranging from 100-170°, a residue consisting of the oil heavier than water remaining in the still. The distillate so obtained consists of a mixture of oils having boiling points from 65-170° and sp.gr. from 0.860-0.910, the mixture constituting the material of solvent value. When the composition is to be used as a varnish, the proportion of pyroxylin to the oil may be from 3-10% by weight, preferably about 5%. For a plastic composition to be molded into combs, balls, and other articles about 40-60% by weight of pyroxylin may be used. The tar of hard woods above referred to is obtained from the body of the tree or from both body and bark, as distinguished from the bark alone. The odor may be partially masked, and the color, which is light yellow—entirely removed, by distillation with ferric, stannous or cupric chlorides, in from 0.1-0.3% amounts by weight, followed by a final rectification in the presence of a small amount of permanganate and phosphoric acid. This product before final purification is sold in the United States under the name of "solvol" or "light solvol," and in France under the name of "lignone." A "heavy solvol," consisting of a fraction boiling above 170°, is to be obtained, but the difficulties in deodorizing and rectifying it are much greater than with the lower boiling point fraction.

2. U.S.P. 718670, 1903.

3. Covering practically the same ground as the patent of A. Seher.

4. U.S.P. 384005, 1888; 428654, 1890; 450264, 1891; 483701, 1892.

5. To the author's knowledge this method has been repeatedly tried and under varying conditions upon a manufacturing scale, and the same proportion of benzine introduced could always be readily determined in the distillate. Furthermore, the distilled product apparently exerted no greater dissolving power than a simple mixture of amyl acetate and benzine.

6. U.S.P. 741554, 1903; see also U.S.P. 410204, 410205, 410206, 410207, 410208, 410209, 1889.

butyl ether,<sup>1</sup> ethylisobutyl ether,<sup>2</sup> methylisoamyl ether,<sup>3</sup> and ethylisoamyl ether.<sup>4</sup> These solvents possess the well-known capacity of ether in an ether-alcohol mixture, with a greatly decreased volatility and which are much less miscible with water, hence readily obtained in the anhydrous state. I. Kitsee<sup>5</sup> suggests dissolving the moist cellulose nitrate by exposure to fumes of the solvent, specifically acetic acid.<sup>6</sup> R. Riddle<sup>7</sup> employs an unflammable solvent directly, phenyl acetate being specified. It, however, is difficult to purify this ester from the phenol usually taken as the source for manufacture. H. Chute<sup>8</sup> fractionates wood spirit, reserves the lower boiling-point portion, esterifies the residue into methyl and ethyl acetates, and mixes with the methyl acetone first reserved. L. Paget,<sup>9</sup> following the idea of Todd, mixes fusel oil (5-8 parts), wood spirit (2-3), and benzene (1-2), dehydrates with calcium chloride and distills with acetic acid, while F. Greening<sup>10</sup> obtains a satisfactory mixed solvent by distilling together ethyl and amyl alcohol with an acetate, laying claim to a higher solvent power than is obtainable by a single mixture of ethyl and amyl acetates. G. Michaelis<sup>11</sup> leads gaseous methyl ether into methyl alcohol, or ethyl ether into ethyl alcohol, or interchangeably a methyl into an ethyl derivative, in the presence of a moderate heat and sulphuric acid, rectifying in the usual manner.<sup>12 13</sup>

1. A pungent smelling liquid boiling at 59° (under 741 mm. pressure). Methyl-*n*-butyl ether boils at 70°.

2. Can be formed (Norton and Prescott, Am. Chem. J., 1884, **6**, 216), by heating molecular amounts of ethyl and isobutyl alcohols. It boils at 78-80°.

3. An ethereal smelling liquid, boiling at 91°. The above three ethers are not direct solvents, resembling in this respect ordinary (diethyl) ether. They are intended to be used in conjunction with an alcohol; those of higher boiling points, with the higher boiling point alcohols separated in fusel oil rectifications.

4. Boils at 112°, and otherwise resembles the above.

5. U.S.P. 767944, 1904.

6. Such an acid compound would be of no value in a lacquer, waterproofing, or artificial silk solution, and would be most applicable in the coating of incandescent gas mantles.

7. U.S.P. 797373, 1905.

8. U.S.P. 845616, 1907; also D. Sutherland and W. McLaren, E.P. 28613, 1896.

9. U.S.P. 494790, 494791, 494792, 494793, 1893; E.P. 7784, 1893. According to the patentee, the liquid is a stronger and more active solvent of both pyroxylin and resins than is a mere mixture of methyl acetate, amyl acetate and benzene. Equally good results, it is claimed, are obtained where ethyl alcohol is substituted for the fusel oil, or benzene or oil of turpentine for the benzene.

10. E.P. 5344, 1889.

11. Phot. Wochenbl., 1896, **22**, 185.

12. The author states that collodion prepared by this solvent is extensively used in America in the manufacture of collodion emulsion paper, and is also recommended for the wet collodion process. The collodion from this methyl alcohol process does not set so rapidly as that prepared with methyl alcohol, it is said, and the plate being coated must therefore be laid in a horizontal position to harden after pouring, otherwise an extremely thin layer will be formed.

13. According to V. Vendar (F.P. 372267, 1906) the cellulose nitrates can be gelatinized by the nitroacetins and nitroformins without the aid of a solvent, and

Cellulose nitrate solutions are either solid, fluid or of an intermediate stage. Where a solid compound results by acting upon the nitrate with a latent solid solvent as camphor, the pyroxylin loses all structural and cellular form and passes into a homogeneous colloidal mass. This solvent disintegration is termed "conversion." A liquid compound may result upon immersion in a suitable solvent, in which state the conversion, although invisible, is nevertheless implied and recognized. This may be experimentally demonstrated by evaporation of the dissolving liquid, leaving a structureless mass, which by no known treatment can be transformed to the physical state preceding conversion. The two terms conversion and solution are therefore synonymously applied to the phenomenon of dissolution of a solid by a liquid. All simple active solvents produce both conversion and solution, that is, a liquid, after having first dissolved a cellulose nitrate, may be indefinitely diluted with the same solvent without throwing the solids out of solution. The solution still continues, irrespective of the attenuation of the solids by continued dilution. There are some essential oils, however, that produce conversion of the pyroxylin, and then throw out their own excess, i.e., no more oil is assimilated than is required for the conversion process, that of solution in the same oil being refused. Both may be induced by mixed solvents (alcohol and ether) neither of which taken separately have dissolving power. There is possible in this instance the phenomenon of dilution of the solution with one of the solvents indefinitely without granulation or appearance of precipitation. Dilution with the alcohol, however, soon reaches an observable limit. In addition to conversion and solution, the factor of dilution enters into consideration in the production of commercial cellulose nitrate mixtures, especially where attenuation is desired. Neither methyl (ordinarily) nor amyl alcohol are solvents of pyroxylin. Statements

this property is made use of for the production of a plastic or a gelatinized explosive. The method of preparation is as follows: Glycerol 100 k. and anhydrous oxalic acid 50 k. are heated together at 140-150° for 20 hours. The product, consisting of 125 k. of a mixture of glycerol and monoformin, is nitrated at 25° with a mixture of 275 k. of strong nitric acid and 90 k. of fuming sulphuric acid containing 25% sulphuric anhydride. The oil which separates is washed with water and a dilute solution of sodium carbonate. It is pale yellow in color, has a sp.gr. of 1.57 and contains 15.7% of nitrogen. This corresponds to a mixture of nitroformin 33%, and nitroglycerol 67%; 100 k. of this mixture will gelatinize from 100 to 400 k. of nitrocellulose, and an explosive of any required degree of plasticity or hardness can thus be obtained. The dinitroacetin compound is obtained in a similar manner to that already described. It has a sp.gr. of 1.45 and contains 12.5% of nitrogen. Gelatinization of nitrocellulose can also be effected by the addition to moist nitrocellulose of a basic acetin soluble in water. If the water is then evaporated, gelatinization of the nitrocellulose takes place, and the resulting plastic mass can be formed into grains or flakes as desired.

appear in the literature where nitrated cellulose has been found soluble in ethyl alcohol and anhydrous ether, but examination of these isolated instances have usually brought out the fact that the products were rather nitrohydrocelluloses, nitrooxycelluloses, or products formed by the nitration of the degraded cellulose molecule, or the purity of the solvents used was open to question. There are isolated solubility anomalies of the cellulose nitrates which are so inexplicable, and results recorded by investigators of unimpeachable veracity so conflicting, that solubility statements of these esters should be accepted with a slight latitude. The author has proven that with a cellulose nitrate of 11.18% nitrogen and entirely insoluble in anhydrous (from metallic sodium) ether, the addition of 1% absolute ethyl alcohol induces 2.6% pyroxylin present to pass into solution, the formula used being 5% by weight of pyroxylin in 100 cc. ether. However, a methyl alcohol containing 5% acetone is a ready solvent, whereas 5% acetone mixed with amyl alcohol, both being equally anhydrous, has no appreciable dissolving effect. Conversely, a pyroxylin solution at the point of precipitation may be indefinitely diluted with amyl alcohol containing 5% amyl acetate without throwing the solids out of solution, whereas the same amount of amyl acetate in a methyl alcohol, acetone-free solution, will soon cause the pyroxylin to be precipitated. If a pyroxylin be dissolved in acetone, the solution may be diluted to any extent with absolute ethyl alcohol without precipitation ensuing, but with anhydrous amyl alcohol antagonistic evidence soon shows itself in a clouding of the mixture. In technical solutions of the cellulose nitrates the solvents are seldom recovered, therefore the limits of safety are usually approached in the various formulas made, on account of the fact that in general, the non-solvents are much less expensive than the solvents. Therefore it is evident that statements of the solubility of a specific cellulose nitrate in mixed solvents only have a distinct significance when the degree of absoluteness of the individual solvents are specified and the proportions in which they are present stated.

**Classes of Solvents.** The solvents of pyroxylin may be rationally divided into (1) those which dissolve directly without pressure or the application of heat as acetone and amyl acetate; (2) those which require heat or pressure or both as camphor or naphthol, and which are usually spoken of as latent solvents; (3) combinations of two or more bodies, either of which separately exert no solvent action; e.g., alcohol and ether, calcium chloride and ethyl alcohol; and (4) combination of a solvent with undesirable physical properties (hygroscopicity of acetone) with a nonsolvent which will overcome the same (amyl

alcohol) and produce a desirable whole. To the third class, the term indirect solvents has been applied.

Subdividing solvents according to their chemical composition, it will be noted that all the liquids which have stood the test of time are members of the aliphatic (paraffin) series of organic derivatives. Those carbocyclic (benzene) derivatives are, with the possible exception of nitrobenzene, all solids (phenol, dinitrobenzene, coumarin, naphthols, naphthylamines, benzanilid, etc.). The alcohols, ethers, ketones and esters of the hydrocarbons methane, ethane, propane, butane and pentane, comprise all the solvents of practical value. Certain halogen-substituted hydrocarbons (chloroform, carbon-tetrachloride, pentachlorethane, etc.) are useful in connection with the cellulose acetates, but do not dissolve the nitrates.

None of the alcohols or simple or compound ethers in their pure state are solvents. Any simple alcohol mixed with any ether exerts a decided solvent action. The acids are all solvents, the avidity of solution rapidly diminishing with increased molecular weight. Formic acid is an example of the general observation that the first member of a homologous series does not deport itself like the succeeding members, and in this it is no exception to the rule. The acids are enabled to dissolve pyroxylin and to retain it in solution upon dilution with a larger amount of water than any class of compounds, acetic acid being conspicuous in this respect, and holding pyroxylin in solution when as much as 18% water is added. The alkyl esters (methyl, ethyl, propyl, etc., formates, acetates, propionates, etc.) are all active direct solvents, their activity, instability and commercial value and cost of production decreasing with increased molecular weight (from methyl acetate to amyl acetate) of alkyl, and activity, desirability and cost increasing each way from the acetate with the same alkyl. The normal esters are apparently more energetic solvents, normal propyl acetate being a better nitrocellulose solvent than the *iso*acetate, while ethyl *isovalerate* is stated to be more efficient in this respect than ethyl valerate. The formates or propionates, although excellent solvents and which would be used in immense quantities annually, have received only scientific interest on account of cost of the raw material required in their formation. The simple and mixed ethers higher than ordinary sulphuric ether (diethyl oxide) have never been used to any considerable extent. This is not true of the higher ketones, which in their partially purified form enter into commerce as the acetone oils, and find extensive use. No aldehyde with the possible exception of benzaldehyde has gone beyond the experimental stage as a pyroxylin solvent.

for waterproofing purposes, being thin sateen or similar other cotton cloth, upon which has been deposited a pyroxylin solution high in castor oil, and usually containing powdered aluminum or other metallic bronze. The compounds of Bonnaud<sup>1</sup> were practically heavy pyroxylin-resin lacquers, the resin being usually copal. The mixture was applied hot in order to insure thorough permeation of the fibers of the cloth. Ramie, jute and other vegetable fibers were used to produce the heavy and cheaper grades of cloth. The electric wire insulating compound of Castle<sup>2</sup> is a cellulose of low nitration dissolved in acetone, and thickened with locust bean flour. To prepare gloves or other articles of dress for protecting the wearer against injury from X-rays, Saunders and Craske<sup>3</sup> first soak the fabric in a solution of lead nitrate, or use a saturated solution of lead acetate in ethyl alcohol as a component of the cellulose nitrate mixture, which is then applied to the cloth in the usual manner. Similarly prepared fabrics have been used as a protection against the emanations of radium. Where waterproof materials are not soft enough, even with the addition of the maximum amount of castor oil, 40% or 50% of the methyl or ethyl ester of sebacic acid may be added to the nitrocellulose solution.<sup>4</sup> But the present market price of methyl or ethyl sebacate, unless in a very impure form, would appear to preclude its use to any extended degree for this purpose. The waterproofing solutions in general are applied in a manner similar to the described processes for the manufacture of pyroxylin-containing leather. In the preparation of dress shields intended for insertion in the armpits to retard outward appearance of perspiration, a thin, finely woven muslin is usually taken for the background, and to give extreme flexibility, an equal weight of castor oil is added to the cellulose nitrate before application. After coating, the goods are usually passed through a calender with friction rolls to give the coated fabric a smooth appearance and high gloss.

Stevens<sup>5</sup> has drawn attention to the fact that those waterproofing compositions containing castor and non-drying oils—and they form the major portion of the preparations now in use—have a tendency to turn rancid upon standing, and this rancidity imparts to the fabric an objectionable odor and in time affects its strength. He has sought to improve such fabrics by the introduction of new elements into their combinations, whereby tendency to turn rancid is diminished. Carbolates and sulphocarbolates as alkali salts,<sup>6</sup> zinc chloride, bromide, iodide, and chlorate, mercuric chloride,<sup>7</sup> and sodium

1. U.S.P. 697790, 1902; E. P. 8063, 1901.

3. E.P. 27357, 1904.

5. U.S.P. 612066, 615319, 621382, 622727.

7. U.S.P. 612066, 1898.

2. E.P. 2167, 1904.

4. G. Z. Suppl., 1907 (July 19), 91.

6. U.S.P. 612553, 1898.

benzoate and salicylate,  $\beta$ -naphthol<sup>1</sup> and naphthalin<sup>2</sup> are among those chemicals stated to produce satisfactory results. The method of use is to dissolve the deodorizer or antiseptic in amyl acetate or alcohol and combine with the formula in the usual manner. Stevens submits as a satisfactory formula, pyroxylin 100, castor oil 150, camphor 150, zinc chloride 3, and wood spirit sufficient to thin the mixture so it will spread. Sulphocarbolate of soda is stated to be especially beneficial in this respect, used in quantities of 4% of the weight of the pyroxylin employed. Where transparency is of no importance,<sup>3</sup>

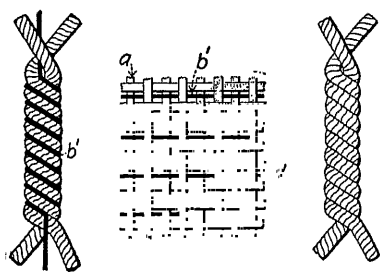


FIG. 119.—Waterproof Cloth According to A. Kennedy.

potassium, sodium or lithium salicylates are advised, and zinc benzoate, salicylate or sodium  $\beta$ -naphtholate where color is of no moment. The method of A. Kennedy<sup>4</sup> consists in entwining or interlacing regular or ordinary threads along with extra strands or fibers of nitrocellulose (Fig. 119), thus forming a textured article, which when subjected to the action of a solvent of the

nitrocellulose, causes the dissolved pyroxylin to impregnate the regular fibers, thus producing the waterproof effect.

**Enameled Paper. Wall Coverings.** In order to produce in wall papers the appearance of silk, satin or horseshair fabrics, ordinary heavy paper is coated with a nitrocellulose solution in a manner similar to the coating of cloth for artificial leather, a small amount of castor or raw linseed oil being added.<sup>5</sup> When dry the coated paper is passed through an embossing machine the rollers of which run at equal or unequal speeds according to the effect required. It may also, before being embossed, be passed through a friction or glazing calender. If the embossing press is engraved with very fine flutes, a silky gloss or effect is made possible on the covered surface.<sup>6</sup>

"Fab-Ri-Ko-Na" is the trademark name for a line of woven wall coverings, which includes dyed and undyed burlaps, canvas, crash and other cotton goods. The dyed burlaps are in plain, solid colors, or printed in various designs. The undyed burlaps are given special fillings and surface treatment, and are intended to receive oil or distemper paint after they are hung. Some of the cotton fabrics are for

1. U.S.P. 622727, 1899.

2. U.S.P. 615319, 1898.

3. U.S.P. 621382, 1899.

4. U.S.P. 590842, 1895.

5. W. V. Wilson, E.P. 6051, 1884; 491, 4668, 1885.

6. W. L. Wise, E.P. 18374, 1900.

painting on, where others are for lining walls where a lining is needed as a foundation for other wall coverings. All the goods are given a backing which is made to receive ordinary flour paste, and they are hung similar to wall paper. Containing no pyroxylin, these products are, therefore unflammable, and have both the face and back impregnated with a non-poisonous, odorless, antiseptic substance. "Cott-A-Lap" and "Tex-Ta-Dor-No" are similar.

Aluminum, gilt and the various colored bronzes are especially applicable as materials for the coating of paper, principally due to the fact that a thin layer can be applied to the paper and still have the finished preparation entirely opaque. If the paper backing has the requisite strength, the finished material may be embossed in raised work by means of a plate embosser and artificial heat. Usually but one coating is given the paper, the bronze being incorporated in the coating composition before spreading. It is a peculiar fact that aluminum in combination with cellulose nitrate—the latter being in solution—is very prone to gelatinize upon standing, so that paper cloth intended to be coated with aluminum must have the composition applied soon after made, or the material solidifies, after which no combination of solvents will render the material sufficiently soluble to admit of again spreading with uniformity.<sup>1</sup> Another method resorted to less frequently is to cover the paper with a transparent pyroxylin coating, after which aluminum or other metallic powder is sifted on the wet surface and before the latter has had time to harden. After passing under rolls to imbed the metal in the coating composition, the paper passes over steam-heated drums until dry, when the superfluous powder is removed mechanically. Snow and other brilliant effects are produced by substituting for, or using with the colored bronzes, powdered mica, quartz, garnet, and ground crown and prism glass, the scintillation of the latter making more conspicuous the metal and bronze portion.<sup>2 3</sup>

Enameled paper in which the waterproofing portion is pyroxylin or celluloid has been in active demand for many years as coverings for confectionery boxes and similar uses, and the paper is impregnated or enameled with the cellulose nitrate usually in one of the three following ways:

1. H. Heil and E. van den Kerkhoff (D.R.P. 217852, 1908) claim that these difficulties can be obviated by using cellulose nitrate soluble in alcohol, and dissolved in absolute alcohol or alcohol of high concentration.

2. For descriptions of machinery and processes for pyroxylin coating of paper see S. F. Piehler, E.P. 9261, 1894; F. E. Ullstein, E.P. 5657, 1885; E. Bush, E.P. 9624, 1895; 22674, 1898.

3. For description of other methods of coating paper see T. Fritsch, E.P. 6590, 1906; Vellumoid Paper Company, U.S.P. 740006, 1903; E.P. 19541, 1903; abst. J.S.C.I., 1903, 22, 1145.



Where celluloid is used in the solid form, it is preferably first ground in water to the desired fineness for the particular paper to be made, but not dissolved. The wet celluloid and moist paper pulp are then thoroughly mixed until either component is indistinguishable to the naked eye. After the combined pulp-celluloid paper has been formed into rolls in the usual manner, and has passed through the last of the heated rollers used for the removal of the water, the paper may either be passed through a calender roll heated to 145–160° with great pressure in order to soften the celluloid and amalgamate it with the paper substance, or the paper may be put through a vapor bath of alcohol spray, the object of the latter process being to sufficiently dissolve the superficial celluloid to produce the waterproofing and enameled effect. In order to economize on alcohol solvent used, the two steps may be combined, and heated rollers used at first, this being followed by the alcoholic vapor or spray to integrate what material has not been affected by the heated calender rollers. By this method<sup>1</sup> the paper is waterproofed and enameled as well. The proportion of celluloid to paper will depend upon the uses to which the finished paper is to be put.

In the method of J. Edson<sup>2</sup> sheets of paper and celluloid are rolled together between compression devices, being subjected to a spray of solvent just before they are pressed together. In order to produce enameled paper or fabrics of two or more colors, M. Bogert<sup>3</sup> first submerges the paper or fabric in a pyroxylin solution of convenient concentration as regards the nitrocellulose, and after the paper or fabric has been subjected to slight pressure to remove the majority of solvent, small pieces of celluloid in stars or other shapes are placed over the soft surface, the latter being then subjected to heavy roll or press pressure in order to imbed the colored pieces in the yielding celluloid substance. After the solvent has entirely evaporated the goods are passed through friction rolls to increase the polished appearance. Care must be exercised that the solvent be nearly all removed before the colored designs are attached or the color in the latter may sufficiently dissolve out to impart a blurred appearance due to the indistinctness of the partially dissolved patterns. Such materials are admirably adapted to be used in the manufacture of pencil cases, card cases, jewelry, watch and toilet cases, book and album covers, and similar uses.

In the P. Reid and J. Eastwood method of topical printing<sup>4</sup> the distinctive novelty of the invention consists in the employment of a

1. Process of W. Carpenter, U.S.P. 251410, 1881; 253840, 1882.

2. U.S.P. 290553, 1883. 3. U.S.P. 270538, 1883. 4. U.S.P. 256597, 1882.

pyroxylin solution for the purpose of "setting" or "fixing" the design, the impression being delivered by means of pressure or by bringing a surface having a "color" applied to it in direct contact with another surface upon which the impression is intended to be made. Previous to this invention it had been necessary to apply heat or other treatment after the printing operation, in order to fix or set the color upon the surface which had received the impression. The employment of a pyroxylin solution as the binding material to secure the mechanical attachment of pigments to surfaces upon which impressions have been made enabled any subsequent treatment to be dispensed with after the mixture had been applied to the surface by printing. The pattern was placed on an enameled or waterproofed paper or textile by a method quite similar to direct printing, except the ink was replaced by a colored pyroxylin solution.<sup>1</sup> Rollers, types, blocks or other agents are suitable for delivering the impression, the pyroxylin composition, in general, consisting of pigments or dyestuffs ground or dissolved in a slowly evaporating cellulose nitrate composition, e.g., one high in fusel oil and amyl acetate. The veneer cloth<sup>2</sup> and enamel cloth<sup>3</sup> of J. Stevens and W. Wood is based on the same principle as above.

**Printing on Fabrics with Pyroxylin.** The Lilienfeld method of producing impressions fast to water<sup>4</sup> is to combine pyroxylin with organic esters of high boiling-point—ethyl phthalate being specified—and apply this to the cloth in any suitable manner. Instead of evaporating the solvent from the cloth after passing under the coating knives the coated fabric is passed between two rollers, one or both of them being engraved with lines. These rolls are heated nearly to the boiling temperature of the solvent used, so that after having passed through the rollers the fabric will assume a stiff form before the embossing disappears. The major portion of the solvent is vaporized at the moment of contact with the engraved rolls and the surface of the cloth assumes the form corresponding to that of the surface of the roller, thus producing a sheen and shimmer to the finished fabric, especially when viewed at an obtuse angle to the source of light.

**Imitation Textiles.** In order to imitate damask for table-cloths, napkins and fine linen, according to the process of E. Heusch,<sup>5</sup> the textile material is covered with a nitrocellulose solution containing a small amount of castor oil to impart the desired flexibility, after which the coated cloth is embossed by engraved rollers in such a manner as to produce the appearance of damask on the surface. Artificial brocade may be prepared by the method of F. P. Werner<sup>6</sup> by moisten-

1. See J. E. Brandenberger, F.P. 405430, 1908; E.P. 24811, 1908.

2. U.S.P. 297098, 1884.

3. U.S.P. 329093, 1885.

4. E.P. 592, 1907.

5. E.P. 22391, 1899.

6. E.P. 22262, 1891; see R. Kron, E.P. 13112, 1902

ing a woven fabric with gelatin and pyroxylin both dissolved in glacial acetic acid. It is then coated with a paste containing pigment and cellulose nitrate in solution, together with Venice turpentine, the whole being painted on with a brush. When dry, the final coat is applied by brushing over the surface an amyl acetate lacquer containing a small amount of boiled linseed oil. Subsequently the fabric is covered with leaf metal, either real or imitation, followed by an alcoholic shellac solution to aid in the adhesion. This surface can be embroidered, painted or printed on for producing upholstery and other coverings.

A process for the formation of artificial velvet devised by F. Kuhlmann<sup>1</sup> has recently been placed on a manufacturing scale in England, and consists of applying wool dust or cotton dust to a paper or cloth surface by means of a pyroxylin cement, or to a cotton or linen fabric to imitate woolen. The wool or cotton may be dyed before or after application. Similarly, imitation of Brussels and other carpets has been attempted by adding cotton and woolen dust or flock to a backing of burlap or other heavy material, the adhesive being a composition similar to that used in artificial pyroxylin leather. The woolen or cotton is sifted on the surface freshly covered with pyroxylin, then passed between rollers to imbed the material in the adhesive composition, when after drying the coated cloth passes through heavy brushes which raise the "nap" of the carpet. A silky appearance may be given to closely woven shirting or other cheap fabric of cotton or linen according to the claims of Thompson,<sup>2</sup> by means of metallic powder in an extremely divided condition applied warm with "zapon lacquer." The success of the product depends upon applying but a minute portion of the metal—just sufficient to give to the goods that silvery appearance similar to mercerized cotton. In metallizing yarns or hosiery made of textile fibers,<sup>3</sup> a mobile solution of cellulose nitrate in ether-alcohol has been advocated. The metallic powder is suspended in the liquid, and the yarn dipped in the solution. After thorough drying the process is completed by an immersion in a pyroxylin solution to which no metal has been added. Watered effects are possible by slightly dampening the fabric by means of a spray of a 4-5 oz. cellulose nitrate solution in a readily volatilizable solvent as methyl alcohol or acetone, and then passing between heated rollers, one or both of them being engraved with lines. The solvent being vaporized at the moment of contact with the heated rollers, the surface of the

1. E.P. 320, 1855.

2. E.P. 13485, 1904; for process of obtaining iridescent textiles see Joly, F.P. 350041, 1904.

3. A. Forster, E.P. 24289, 1903.

cloth will permanently assume the form of the roller. The insolubility of the sprayed lacquer in water produces effects not altered by exposure of the fabric to dampness. For moreens, in which the rib of the cloth runs in the direction of the warp,<sup>1</sup> the lines on the roller are cut circumferentially; whereas for moirettes and poplins, in which the rib runs weft-wise, the lines are engraved parallel to the axis. For watered designs, the lines, instead of being continuous, contain the design engraved in relief on the roller, and the face of the design is then engraved with lines at such a distance from each other as harmonizes best with the rib of the fabric.

According to F. P. Werner<sup>2</sup> a substitute for or imitation of brocade, free from the liability of the metal to chip or rub off, may be produced as follows: The fabric is stretched smooth on a frame, moistened with gelatin, and dried. The surface is then brushed over with "leather collodion," and again coated after drying with "French mixture" or gold ground in oil, which is sprinkled over the surface very lightly. Any suitable pattern may then be stamped on the surface. M. Ratignier and H. Pervillae<sup>3</sup> make artificial lace fabric by discharging collodion upon a roller, the face of which is engraved with grooves of lace pattern, the surplus material being removed, and that retained in the grooves hardened by chemical treatment or evaporation before removal from the roller.

According to J. and B. Galay<sup>4</sup> paper, glass, or other materials may be coated with a mixture of collodion and powdered metal by applying the fluid mixture to the surface of the material in a closed chamber or discharging it from a closed vessel through a slot. The coated material is then passed through a trough, in which a stream of water flows in an opposite direction to the travel of the coated material. The water absorbs the solvent of the collodion and fixes the film, the solvent being recovered by distillation. The thickness of the film may be varied at will, either by rolling it under water whilst the collodion is still plastic, or else by conducting the material from the coating vessel to the water trough at a suitable angle of inclination, so that the excess of the coating mixture flows back to the vessel.

**Artificial Leather Cements.** To unite sheets of coated cloth in the formation of larger pieces, to mend leather and cloth belts not subjected to high tension, and to repair pyroxylin-containing articles, various adhesives have been suggested. The most successful have

1. J. and S. H. Sharp, E.P. 21590, 22056, 1906; 7382, 7749, 1907.

2. E.P. 22262, 1891; in the haircloth fabric of G. Goldman (U.S.P. 840841, 1907) zinc resinate is the adhesive.

3. U.S.P. 934214, 1909.

4. E.P. 19772, 1909.

consisted of a pyroxylin solution (12–16 oz.) containing 3–4 oz. camphor, and low in solvent power. The latter property is necessary in order that the cement will not deeply penetrate the coated material, and render it soft and slow in drying. In order that this class of adhesives shall act quickly, the solvents are all low boiling (acetone and wood alcohol), and as little as possible of the pyroxylin solution is used, heavy pressure after application being beneficial. The preparations of S. Barnwell and A. Rollason,<sup>1</sup> T. F. Gillot,<sup>2</sup> and J. H. Drinkwater<sup>3</sup> have consisted of “xylonite varnish”—combinations of pyroxylin with india-rubber, resins or linseed oil, and shellac partially saponified with borax. A preparation of a 6 oz. pyroxylin in amyl acetate 55, fusel oil 12, acetone 10, and benzine 23, mixed with 5 oz. india-rubber in 7 oz. carbon bisulphide is said to be very adhesive, and has been used to attach tires with satisfactory results. Carlton Ellis<sup>4</sup> has produced a preparation fairly representative of this class of adhesives, consisting of 10 lb. nitrocellulose dissolved in 8 gal. acetone, 1 gal. amyl acetate, and  $\frac{1}{4}$  gal. creosote, to which 4 lb. camphor is added. The creosote may be intended as a deodorizer, an unusual constituent in a cement of this character. The two pieces of textile or other material which it is desired to join are laid together, a small amount of cement brushed on, pressure applied and continued if possible until the solvents have nearly evaporated, when the pressure is removed and the cemented surfaces allowed to harden in the air. Where the pressed pieces are joined before embossing, the pressing of the pattern renders the cemented edges practically invisible.

A preparation known as “Universal Belt Cement,” and to be obtained on the market, is a thick, heavy-flowing liquid, colorless, consisting of pyroxylin 12%, camphor 5%, amyl acetate 40–45%, refined fusel oil 5%, acetone and wood alcohol 40%, and is said to give excellent satisfaction. The ends of the belt to be joined are shaved smooth, the cement applied, and the edges pressed or hammered together and fastened until the cement has become dry.

1. E.P. 2249, 1860.
3. E.P. 2625, 1872.

2. E.P. 1746, 1866.
4. U.S.P. 778232, 1904.

## CHAPTER XII

### PYROXYLIN-COATED ENAMEL AND PATENT LEATHERS

At the risk of incurring adverse criticism, it is the author's conviction based upon experience, that the coating of leather with the cellulose nitrates, as at present carried on in the United States at least, has not placed itself on anything like a satisfactory scientific basis. And this is primarily due to the fact that the entire tanning industry seems to be permeated with (to say the least) a degree of reticence, coupled with apparently irrational and scientifically inexplicable individual methods and rule-of-thumb processes, which at the present time make attempts to reduce the pyroxylin coating of leather to an exact and logical basis very difficult, if not wellnigh impossible. The cellulose nitrates are applied to the tanned skins and leather only in the condition in which the latter are presented; on *a priori* grounds, therefore, it is evident that if the preliminary steps of tanning and finishing are not reduced to a somewhat generally accepted uniform system of procedure for the various classes and conditions of skins, definite and concordant results in subsequent pyroxylin coating are impossible. An immense amount of intelligent experimentation and a high degree of theoretical and manipulative skill have been brought to bear on the choice of solvents and selection of nitrocotton; it is possible to produce a pyroxylin solution where the solubility, viscosity, total solids and speed of evaporation are under entire control and can be duplicated indefinitely; therefore the frequent lack of uniformity of results obtained in leather coating must be mainly attributable to the varying nature of the skin and its treatment in the processes of leather formation.

The coating of leather with pyroxylin is comparatively recent.<sup>1</sup> In the United States census returns for 1900 no mention is made of the application of nitrocotton to leather. It is within the past ten

1. An idea may be gained of the (practically) entire absence of information on this subject from the fact that the following works contain no mention of the application of pyroxylin to leather: Proctor, "Leather Manufacture," 1903; Trotman, "Leather Trades Chemistry," 1908; Watt, "Leather Manufacture," 1906; Flemming, "Practical Tanning," 1909; Bennet, "Manufacture of Leather," 1910.

years that this art has passed out of the experimental stage, while to-day it is firmly established as a distinct industry. The advent of the "hide splitting" machine, whereby a skin is cut into two or three sections, each of the size and shape of the original, has done much to give impetus to leather coating, because it has made available a large number of hides of inferior quality which it was found could be greatly improved in appearance and lasting qualities by treatment with nitrocellulose solutions. The three centers of industry in the United States at present may be stated as Newark, N. J.; Bristol, Pa., and the vicinity of Philadelphia, and Boston, Mass. At Newark the majority of hides treated are the so-called "splits" and chrome tan leather.

The object of tanning hides, kips and skins<sup>1</sup> is to render the animal skin imputrescible and pliable, and to indefinitely preserve it. At the present day, as leather is rarely used with the hair on, preliminary processes are first needed to remove the hair and to prepare the skin for the subsequent tanning processes. The skin is usually first washed to remove dirt, blood and salt, the removal of the latter restoring the skin in a great measure to its original soft and permeable condition. The hair is loosened by softening and partial solution of the epidermal structure in which it is rooted. This is accomplished usually by soaking for some days in a milk-of-lime solution whose action may or may not be facilitated by the addition of alkaline hydroxides or sulphides. When the latter are used exclusively and in concentrated condition, the hair as well as the epidermis is softened, or if the solvent action be continued, is entirely dissolved and destroyed. In addition to loosening the hair, it is claimed the lime swells and bursts the fiber bundles of which the hide tissue is composed, making the latter in a more receptive state to receive the tannin. The lime also saponifies any fat present, which is afterwards removed as the calcium salts of the fatty acids.<sup>2</sup>

1. Animal skins are divided into (1) hides, or the skins of the larger and full-grown animals as ox, cow, bull, buffalo, horse; (2) kips, or the skins of the smaller animals of the bovine class; (3) skins, of the smaller animals, as calf, goat, deer, sheep, fox. Kip is a name also applied to a tanned split skin of a weight between that of a calf and a light hide. The quality of hides and skins is greatly influenced by the conditions under which the animal has grown, the nature of its food, the variety of breed, climate and state of its constitution, its age and the time of year when it is slaughtered. The hides of the larger oxen form, when tanned, a stouter and heavier leather than those of cows, especially if the latter are from old animals or from those which have calved several times. The hides of bulls are of coarser grain and thinner in the back or butt, than those of oxen or heifers or young cows, although they are stouter in the neck and certain parts of the belly.

2. For some purposes a distinct putrefactive process is substituted for the liming, the skins being hung in a moist, warm chamber until the soft mucous layer forming the corium or inner epidermis partially disintegrates by simple putrefaction, sufficiently so that the hair may be scraped off. In this case the hide fiber is not

The hair, after loosening, is scraped off with a curved handle blunt knife on a partially rounded sloping board called a "beam," the operation being termed "depilating" or "unhairing."<sup>1</sup>

This is usually followed by "fleshing," which is a similar treatment of the other side of the skin on the same beam, and with a similarly shaped knife, which however, is two-edged and sharp. All of the true flesh, fat and loose tissue, is carefully removed by scraping and cutting, fleshing machines being largely used for this purpose. For sole leather the skin, after thorough washing in soft water to eliminate all traces of lime, is then ready for the tanning process proper. For the softer and finer grades of leathers a more thorough treatment is given for removal of the lime, and so increase the pliability of the skin by solution and removal of a portion of the intercellular tissue.

This fermentative and putrefactive process, the most common form of which is known as "bating," consists in steeping the hide for a number of days in a fermenting infusion of pigeon- or hen-dung. While the theory of its action is not understood it has been ascribed to the unorganized enzymes elaborated by the bacteria present. The effect is the removal of the lime by the weak organic acids formed, the partial disintegration of the cuticular fiber, and the skin—which upon treatment with lime has become plump and swollen—rapidly becomes relaxed and flabby.

In the lightest weight leathers, such as kid and lambskins for gloves, and goat and sheep for moroccas and cordovans, dog-dung is substituted for that of fowls, when the process becomes known as "puering." If the lime has not been entirely eliminated, a subsequent treatment called "drenching" is resorted to. This comprises either soaking the skins in a fermenting bran infusion in which the small quantities of acetic and lactic acids formed exert a solvent on the lime, or more recently of treating the skins directly with lactic acid, alone or in conjunction with acetic acid. The next step is the tanning process proper, which consists in soaking the pelts in a series of tannin extracts or infusions, commencing with a weak solution and increasing the strength of tannin, until examination of the skin shows that the penetration has been complete and the cuticle and corium converted into an insoluble compound of albumen or gelatin with tannin, from which neither component can be regenerated. With heavy pelts the final process is often to dust the moist hide with a powdered tannin

swollen and the swelling has to be induced by a distinct process. This method, if carried too far, results in the complete disintegration of the skin and the formation of a leather very low in tensile strength.

1. The above facts were taken from "Leather Manufacture," H. R. Proctor, 1903.



containing compound, to obtain the maximum of penetration. In the case of sole leather this process, carefully conducted, may require as long as twelve months for successful completion, in order that the hide may be evenly and thoroughly permeated without wrinkling. The leather is then washed free of uncombined tannin, dried and compressed, when it is ready for use.

Dressing leathers, due to their decreased thickness, are tanned in much less time than sole leather, the subsequent filling with fats and oils, which together with the mechanical manipulation constitute "currying." A final film of grease distributed over the surface of these leathers increases the pliability and makes them nearly waterproof. Morocco and other lighter fancy leathers are dyed and submitted to many complex processes before they are offered to the trade, which enhance their value, improve the appearance and increase their durability. Many skins such as calf, glove and glacé kid, are "tawed" instead of tanned, by treatment with a solution of alum and salt, often supplemented by mixtures of flour and albumen to fill and soften the leather.

"Wash leather" or so-called chamois, and leather used for buffing, are produced by fulling the skin with fish, degreas, or whale oil, which converts the skin into leather by subsequent oxidation and at the same time oxidizes the skin to a readily pliable condition.

**Past Processes for the Ornamentation of Leather.** In 1882<sup>1</sup> J. Epstein published his process for producing the appearance of oxidized copper or bronze on leather, usually called "patina." The leather, previous dyed, embossed and grained, is coated with a lacquer containing nitrocotton and a resin, in which the dyestuffs are in solution. To produce a blending of the colors, a portion of the varnish is removed when only partially dry, by rubbing with oil of turpentine. O. Lindner<sup>2</sup> has endeavored to imitate the markings on crocodile skin on leather, by covering the surface with a moderately concentrated solution of glue in acetic acid together with an oil paint, and then drying this coating in a sufficiently rapid manner to cause it to shrink and become cracked, as in the natural skin. A final coat of pyroxylin is applied to form a transparent and tough protective coating. A liquid compound to facilitate the marking of patterns on leather through a perforated stencil for embroidery, may be made<sup>3</sup> by means of a thin pyroxylin lacquer containing a pigment or bronze, oil of bergamot, patchouly or safrol being added to impart an agreeable odor. To place a design, picture, crest or monogram on leather,<sup>4</sup> the design is

1. E.P. 6152, 1882.

2. E.P. 3645, 1886.

3. According to L. Whitefield, E.P. 2123, 1887.

4. T. Stevens, E.P. 4833, 1887.

first woven or otherwise constructed and affixed to the leather by means of a thin pyroxylin cement aided by pressure. After drying, a thin celluloid film is placed over the entire design, the leather having been first moistened with amyl acetate. Pressure is again applied, whereby the superposed celluloid layer is rendered invisible, and the design firmly fixed to the leather. The polished surfaces prepared by P. Meissner<sup>1</sup> by coating leather with celluloid sheets and submitting them to great pressure at a temperature just high enough to soften the celluloid, were highly polished, but they readily separated from the leather on frequent bending. An ingenious machine has been devised for continuously applying gold or silver leaf in strips or bands to leather,<sup>2</sup> consisting essentially in an endless roll over which the leaf passes, where it meets the leather just previously moistened by a thin lacquer. Immediately after the union of the leaf and leather a steam heated pressure roll is encountered, which imbeds the leaf in the leather and at the same time vaporizes the lacquer solvent. The waste paper from the back of the leaf is carried away by means of drawing rollers. To give leather articles the appearance of enameling,<sup>3</sup> they are partly or wholly covered with so-called "silver paper," either plain or embossed with a design. The paper is affixed by pyroxylin and covered with a celluloid sheet. In another method<sup>4</sup> the dressed and pumiced leather is coated with a mixture of 12 oz. pyroxylin dissolved in a gallon of amyl acetate, containing dyestuff or pigment, to which is added 10 oz. lanolin or wool-fat. The finishing coat consists of the above mixture with the lanolin omitted. No wool-fat, to the author's knowledge, is used in leather-coating compositions at the present time.

**Earlier Methods of Coating Skins with Pyroxylin.** As far back as 1861, A. Rollason, as the result of experiments on varnishing leather, obtained a patent<sup>5</sup> for a "collodion composition" to be applied to leather to give it a glazed or varnished appearance.<sup>6</sup> After the failure of Parkesine, Parkes turned his attention to other possible sources of collodion application, and devoted considerable time to the coating of leather and furs. In his patent of 1881<sup>7</sup> there is described a process whereby the leather is first treated with a solution of cellulose

1. E.P. 12870, 1896.

2. L. Bracher, W. Collyer and J. Cassells, E.P. 25369, 1896.

3. J. Herz, E.P. 758, 1897; E. Deiss, E.P. 5837, 1903.

4. Marsden Co., E.P. 17602, 1897; U.S.P. 587097, 1897.

5. E.P. 2143, 1864.

6. He combined collodion with flexible gums as elemi and animi, brushing the mixture on polished glass or metallic surfaces, and then applying the dried film to the leather with friction.

7. E.P. 983; U.S.P. 265337, 1882 (A. Parkes only U.S. Patent).

in zinc chloride or iodide, after which a nitrocotton mixture is applied. It was found, however, that the leather coated by Parkes' method rapidly became brittle and lost its tensile strength, so that the process never developed into commercial importance. In connection with Daniel Spill's American zylonite patents, J. Edson in 1883<sup>1</sup> described that which may be regarded as the first workable method published for the combination of pyroxylin with leather, in which a definite process of attachment of a nitrocotton film is given. Edson first prepared a film of the cellulose nitrate with or without camphor, by allowing a fluid solution to dry on a glass plate protected from dust. The leather was moistened with a pyroxylin solvent, and that side of the film not adhering to the glass attached to the leather, great pressure being exerted. In this manner the leather was covered with a highly polished, water-repellent coat of great beauty and durability. Investigators immediately elaborated on these general principles as laid down by Edson, as to thickness of film and degree and length of time of pressure, pigments, dyestuffs and oils being added to the leather before the film was applied. It was found, however, that the film was inclined to separate from the leather in bending, and this defect could not be satisfactorily overcome. When the pliability of the leather was increased by oiling, the defect became more noticeable. W. Field<sup>2</sup> endeavored to overcome this difficulty by incorporating the oil directly into the film, and this led him to use boiled linseed oil as one ingredient, probably the first attempt to make patent leather with pyroxylin. Although blown corn oil, peanut, castor and rape oils were tried, all appeared to be unsuccessful, the union of film to leather being insufficiently tenacious to meet the trade demands. In order to diminish the antipathy of the oil to pyroxylin, linseed and castor oil were first nitrated,<sup>3</sup> the pyroxylin and nitrated oil being dissolved together in acetone, evaporated to dryness and attached to the leather. In order to induce a more intimate union of pyroxylin and leather the mixture was applied in the semisolid or heavy fluid state, after which a film was attached or a liquid lacquer brushed over the surface as a finishing coat. A. Cohn<sup>4</sup> in 1901, and E. Jetter<sup>5</sup> two years later, made substantial improvements, the first by superposing on the leather a series of coats of varying fluidity and oil content, and the latter by increasing the penetrative power of the lacquer by the partial use of glacial acetic acid. From 1903 until the present

1. U.S.P. 289241, 289338, 1883; E.P. 5554, 1883.

2. E.P. 3460, 1893.

3. W. Reid and E. Earle, E.P. 26677, 1897; see Velvrl.

4. E.P. 16429, 1901.

5. E.P. 4902, 1903.

time improvement has been mainly along the lines of selection of suitable oils to combine with the nitrocotton solution, the adjustment of the composition of the individual coatings, and the nitration of cotton to produce clear and highly flexible films. It was early demonstrated that the nature of the skin and the tanning processes, as governing the porosity of the finished leather, were of great importance in the application of successful coating mixtures, for unless the pyroxylin was enabled to obtain a firm and satisfactory anchorage in the leather substance, application of subsequent coats only tended to pull the first coat away from the leather, and hence weaken the pyroxylin structure as a whole. The importance of the porosity of the leather fiber as a suitable medium for the attachment of pyroxylin cannot be overestimated, and at the present day is one of the most important—if not the unsolved—problem in the successful pyroxylin coating of leather for patent and enamel effects.

**The Process of Field.** The first departure from attempts to attach films to leather which met with any considerable commercial success was the process of W. D. Field,<sup>1</sup> in which a fluid pyroxylin preparation was placed directly on the leather, and which contained a vegetable oil as an essential component. Previous to this the many unsuccessful attempts which had been made in this direction had been due to the impregnation of the leather substance with pyroxylin solutions, with the result that a stiff, horny and non-flexible skin was produced. Applying the experience gained in the coating of cloth with nitrocotton,<sup>2</sup> Field succeeded in obtaining quite satisfactory results with the following process—so far as toughness and pliability are concerned. Corn or cottonseed oil—preferably the latter—is first boiled or “blown” with a siccativ, as antimony pentasulphide, until the proper consistency has been obtained. A solution of 15 lb. pyroxylin in 15 gal. amyl acetate is made, to this being added in small quantities at a time 50 to 60 lb. of the oil blown as above. If pigment is required, it is first ground in a small quantity of the oil before incorporation with the pyroxylin. The material is applied to the leather with a brush or “slicker,” allowing each coat to dry by exposure to the sun or artificial heat not above 40°. The final or varnish coat, much thinner than the preceding, is applied by flowing over the surface, when the skin is left at the ordinary temperature until thoroughly dry. Although the finished product had a disagreeable odor, contained pigment instead of dyestuff which gave a slightly granular appearance to the finished coat, and was of a dark brown rather than a glossy, bloomy black color, Field was the first to produce, in all

1. U.S.P. 627493, 1899.

2. See Chapter XI.

probability, on a manufacturing scale, a flexible, non-penetrable pyroxylin coating on an absorbent, pliable material, which was surface-hardened by a thin, flexible varnish high in nitrocotton, and which proved a commercial success.

**A. Kennedy's Method**<sup>1</sup> modified Field's process in that the flexibility of the leather was increased by applying as the first coat a mixture of pyroxylin, lanolin and corn oil together with coloring matter, preferably in the following proportions: 12 oz. pyroxylin is dissolved in 1 gal. amyl acetate, to which is added 10 oz. lanolin and 3 oz. corn oil. The solution is applied to the leather in the usual way and after drying, a finishing coat of pyroxylin, 10 oz. to the gal., is flowed over to give a more resplendent surface. The fatal defect in this process was the tendency—on long storing—of the corn oil to exude ("spew" or "sweat out") on the surface, either as a greasy opaque bloom or as minute oily drops.

**Enameling Composition of Byron Goldsmith.**<sup>2</sup> In 1909 patent protection was granted for a method of enameling which may be said to embody the most modern patent and enamel leather principles. The linseed oil is first mixed with pyroxylin in solution, and the leather coated in such a manner with one or more layers that the coating last applied is a solution consisting of a solvent of the previous coating. Therefore in building up a plurality of coats the increment of each is "amalgamated" or becomes an integral portion of the last previous coat. A 6 oz. solution of pyroxylin in one gallon of amyl acetate is specified, to which, for the first coat, an equal volume of boiled linseed oil is added. The larger the proportion of linseed oil, the greater the gloss and the softer and more easily scratched the coat. The proportion of pyroxylin is increased from the first to the last coats, the exact number of which will depend upon the fluidity of the solution and the amount used in each separate enameling process.

**The Adams & McKay Process.**<sup>3</sup> This invention relates to the manufacture of that class of enamel and patent leathers where the enameling is applied to the grain side only, and without previous buffing, as distinguished from that class in which the enameling is applied to the flesh or grain side, which has been rendered more receptive and porous by buffing. The process, therefore, is particularly applicable to the manufacture of enamel and patent leathers from light skins as

1. U.S.P. 587097, 1897.

2. U.S.P. 909288, 1909.

3. W. Adams and H. C. McKay, U.S.P. 789249, 1905; the Patent Leather Company of America prefer to use a non-drying oil, as castor or arrack oil, for the inner coat in amounts not less than 30% oil to pyroxylin employed. (E.P. 16598, 1906; F.P. 368383, 1906.)

goat, on which it is often not desirable to apply enamel to the flesh side, nor advisable to buff the grain side.

The process is essentially comprised in two steps, i.e., the degreasing of the leather by means of solvents, followed by the drying oil-pyroxylin preparation. When the tanned skins have been finished to the point where they would otherwise be surface-finished in any of the known ways to make them merchantable, the natural and applied grease in the leather is completely extracted with solvent,<sup>1</sup> preferably naphtha. It is claimed that this degreasing step is essential to enable the pyroxylin varnish to penetrate the grain side below the surface and properly adhere to the inner fibers.<sup>2</sup> Another step in the process which may be profitably employed before the tanned skin is degreased, is a smoothing and compacting of the grain, either by repeated manual application with a slicker, or passing the hide under the glass roller of a glazing machine as though the tanned skin was to be made into glazed kid. The usual "seasoning" with albumen is applied just before glazing. The advantage of the glazing process is the formation of a very smooth and compact surface for the application of the pyroxylin-oil varnish.

In the carrying out of the second portion of the process—the application of the pyroxylin coating—the varnish should be sufficiently fluid to admit of being spread with a brush or sponge, and readily absorbed by the fibrous structure of the grain side without producing an enamel coating. The composition consists preferably of linseed oil boiled to the consistency of fresh mucilage, thinning one quart of this with an equal volume of amyl acetate, or sufficient to give it a density of 31° B $\acute{e}$ ., and then adding a pyroxylin solution consisting of 1 lb. nitro-cotton in 2 gal. amyl acetate. The solvent portion of such a formula is unnecessarily expensive. To each 3 gal. of the above mixture, 1½ oz. nigrosine in 1 quart methyl alcohol is added for the black color. It is claimed that the above composition is absorbed almost instantly by the skin so prepared, penetrating the interior grain surface and enveloping and adhering to the fibers composing the epidermal or grain side with great tenacity. The skins are then either dried in the sun or an oven at a low temperature, and coated with a varnish patented by McKay,<sup>3</sup> which is prepared as described above. It is evident in this process that if a coating of albumen is applied to the grain surface before the pyroxylin, the former will interfere with the penetration of the latter into the leather fiber, albumen not being dissolved by the

1. W. Adams, U.S.P. 685551, 685552, 1901.

2. Pyroxylin and oils being antagonistic.

3. H. C. McKay, U.S.P. 704082, 1902.

pyroxylin solvents named, and hence it would appear that the use of albumen would decrease the adhesion of the nitro cotton, unless a mutual solvent for both pyroxylin and albumen—such as acetic acid—is used. The elimination from the skin, by degreasing, of the oil, which is a direct pyroxylin repellent, is the novel and meritorious invention in the process, and where the proportion of linseed oil is sufficiently large in the first coat to give the desired flexibility, and the solution is sufficiently thin to properly penetrate the fiber, a surface of great brilliancy and strength, it appears, should result.

B. Goldsmith<sup>1</sup> advocates the use of "sized" or "glazed" leather,<sup>2</sup> but increases the adhesion of the enamel coating to the leather by slightly abrading the gelatinous or albuminous surface of the sizing before the pyroxylin coats are applied. This, in practice, may be accomplished by powdered pumice-stone and buffers. The final or enamel coat consists of pyroxylin and a drying oil, preferably 6 oz. of the former to a gallon of solvent, into which has been incorporated 6–9 oz. of oil.<sup>3</sup>

**De Montlord's Film Enamel.** A novel process has recently been proposed<sup>4</sup> of making patent leather by using ethyl acetate as a solvent, the production of which solvent is made possible at a reasonable cost by the use of denatured ethyl alcohol. If De Montlord has succeeded in evolving a process of attaching leather and pyroxylin satisfactorily with ethyl acetate, he has succeeded in a field in which many have worked but all have failed. The ready volatility, hygroscopicity and proneness to acidity of this ester have been the drawbacks which previous investigators have encountered.

The invention consists of a process of making patent leather or artificial patent leather by dissolving nitrocellulose in a suitable solvent with addition of a vegetable oil, alcohol, glycerol, spirits of turpentine, and a pigment or dyestuff, coating either plate glass or aluminum plate, with a composition with from three to five coatings, as may be

1. U.S.P. 783828, 1905.

2. Such leather is made by the application of several coats of albumen or gelatin, in which condition it is known as "sized" leather, or, if after applying the size the surface is polished in a glazing machine, the leather is termed "glazed."

3. In order to save the expense of enameling those portions of the skin which are not used in the finished article and in order to make it possible to utilize the corresponding portions of the sized or glazed leather—that is to say, those portions which would ultimately disappear in scraps after the enameled leather has been cut into its ultimate shape—the sized or glazed leather may be cut into its finished or vamp shape, and then the enameling coat or coats applied in the manner described, to the cut-out pieces. This process is peculiarly useful, because whereas the scraps remaining from cutting up enameled leather into its vamp form have little utility, the scraps remaining from cutting up sized or glazed leather into such forms have considerable commercial value.

4. G. R. De Montlord, U.S.P. 928235, 1909.

required, according to the thickness of either the cotton cloth or the leather to be transformed into patent leather. Each separate coating so spread on the plate is dried by heat before applying the subsequent coating. When the coatings are dry, the leather is then cut in size to fit the plate or the glass on which it is applied, after being immersed in pure ethyl acetate; the leather is then spread on the already coated glass or plate, by means of heavy steel rolls, so that the solution in which the leather is immersed and the coats on the glass or plate adhere strongly together. The plate or glass is then dried with the leather on it, and after drying is carefully removed with the coating and dried again.

When thick, heavy leather is to be transformed into patent leather or several surface coatings have to be applied, it is preferable to apply one at right angles to the other. The leather saturated with ethyl acetate is then spread over the coated plate and by submitting the plate and the leather to pressure, the parts adhere firmly to each other and permit the subsequent removal of the surface coat from the plate.

The following proportions are said to have given good results, viz.: 100 parts of ethyl acetate, aluminum salts, pyroxylin or a similar solution, 4 to 12 parts of nitrocellulose, 2 parts of glycerol, C.P., 3 to 12 parts of castor oil or any other vegetable oil, 10 to 80 parts of pure grain alcohol, 1 to 1 parts of spirits of turpentine, and the pigment or dyestuff, which is thoroughly incorporated in the solution. The proportions, however, have to be varied somewhat according to the thickness of the hides and skins. No details have been obtained as to the success of this process on a manufacturing scale.

**Classes of Leather Coated with Pyroxylin.** There may be said to be two general classes of leather which are pyroxylin coated at the present time in large quantities: (1) split leathers, and (2) leather for patent and enamel wear. The coating of chrome-tanned leather may perhaps be added as a third division.

Hides are usually split on a band machine, where, as its name implies, the cutting is done by means of an endless steel belt which travels with great rapidity over two large pulleys, the edge being kept sharp by the automatic grinding of emery wheels below the machine. In this rather complicated and expensive machine the tanned leather is fed between brass rollers to the knife's edge, the inequalities of the leather being provided for in the under roller by small eccentric brass sections, which in turn press upon a resilient rubber cylinder. If one cut is made, the outer portion is called a "grain split" and the inner, a "flesh split." If two cuts are made, three skins are obtained, an outer very thin layer, known as "buff split," the center portion or



"grain split" and the inner or "flesh split." It is not expedient to attempt the section of a hide into more than three splits, as each portion would then be too thin to be of much commercial value. The value of these splits decreases from the outside inward, except in certain instances where the buff split is so thin as to be useful only for the cheaper class of pocketbooks, satchels and upholstery. Five years ago split leather in the United States was difficult to dispose of, the supply being much greater than the demand. Now the reverse is the case, due entirely to development of the art of applying pyroxylin to the split surface.

In the coating for patent and enameled leather, whole or unsplit leather is usually taken, on account of the rigorous usage to which it must be subjected in shoes and upholstery. Split leather is seldom if ever used in shoe manufacture. The superposing of a series of coats, made necessary in the preparation of acceptable patent leather, makes it advisable to use a strong and heavy leather basis upon which to mordant the pyroxylin, and this is best attained by using the whole leather, without reducing its thickness by splitting.

Chrome-tan leather is usually colored white by processes to be described, although more recently attempts to make patent leather from chrome-tan hides, have apparently been successful. For "Zalol" and other leather cements see Chapter X.

To increase the hardness and resistance to wear, L. Krajewski<sup>1</sup> suggests filling the leather pores and coating solutions with hard bodies (e.g., carborundum, borosilicide) in a very fine state of subdivision. Such material might find favor in upholstering seats in smoking cars to scratch matches on.

**Coating of Buff Splits.** If the outer split from a skin is very light, it is called "light buff," and if slightly heavier, "deep buff." Until very recently the buff splits were simply dyed either with logwood and dimethylaniline, or an acid aniline dyestuff, and glazed by passing the leather through a glazing machine, which distributes a thin coating of egg albumen over the surface, the process being known as "seasoning." Buff splits are so thin as to have but little strength, and this is especially so with "light" buffs, for which reason, formerly but little attention had been paid to their profitable utilization. However, it has been found that the strength can be increased, and the wearing qualities considerably enhanced, by proceeding with this class of leather somewhat as follows:

After dyeing, preferably with an aniline dyestuff in distinction from logwood, the leather is thoroughly dried at a low temperature,

1. F.P. 402460, 1909.

and after cooling, spread out on a large table, and either tacked, or weights placed on the leather to prevent wrinkling. The first coat is placed on the inner or "wrong" side of the buff, and consists in thoroughly brushing in a solution low in castor or linseed oil<sup>1</sup> of which the following formula is representative:

Pyroxylin .....	6 oz.
Commercial wood alcohol, 97% .....	40 fl. oz.
Amyl acetate .....	32 "
Castor oil .....	4 "
Benzine 62° .....	40 "
Refined fusel oil, sufficient to make 1 gal. <sup>2</sup>	

The buff is hung up to dry over steam pipes, where it is allowed to remain several hours, preferably over night. The next morning, or when the solvent has entirely evaporated, the outer or hair side is brushed in the same manner with a thin pyroxylin solution, generally without oil, and seldom over 4 oz. strength. The leather is preferably spread out on a large glass plate, or glass-covered table for this coating application, and left there until practically dry, the last traces of solvent being removed by artificial heat. A satisfactory solution for this treatment would be:

Pyroxylin .....	4 oz.
Commercial wood alcohol, 97% .....	65 fl. oz.
Amyl acetate .....	25 "
Benzine 71° .....	30 "
Refined fusel oil, sufficient to make 1 gal.	

If it is desired to increase the gloss of the outer buff coat—which is usually unnecessary—from 4–12 oz. of boiled linseed oil are added to each gallon of the above formula. The introduction of benzine 71° instead of 62° is made advisable by the larger amount of lighter boiling-point solvent (wood alcohol) as compared with the previous formula. With all thicknesses of this leather except the deepest buffs, it is found that the two pyroxylin solutions penetrate entirely through the leather and anchor to each other, as well as the leather

1. The buff is of so light weight that a pyroxylin without vegetable oil does not make the coated leather too stiff, with the small amount of coating composition used.

2. The fusel oil is necessary to cause combination (physical) between the wood alcohol and benzine, which otherwise would be immiscible. Buff splits from sheep skins are called "skiver."

substance. Such coated buff splits are finding ready sale as material for the better grade of light-weight pocketbooks and the flexible covers of certain books, as loose-leaf ledgers and Oxford bibles. The inner side of these buffs, which is quite rough after coating, is not smoothed, because in all uses to which the buffed leather is placed the inner side is always lined, and hence invisible.

The bands in the inside of men's hats, called "hat sweats," are the buff splits from sheep, calf, or goatskins, calf being the highest in price. These bands are always dyed, but the dyestuff is usually not fast to saline solutions, so that formerly the color would come out on perspiring, and it was not uncommon for a hat band on a hot day to leave a dark streak on one's forehead. Now we see none of this, due to the fact that the buff split used in preparing the band is coated with a thin pyroxylin solution, substantially as outlined above.

In ordinary practice one gallon of solution is sufficient for properly coating 500-600 sq. ft. inner side, or 750-850 sq. ft. outer side, depending upon the thickness and porosity of the leather and the skill and carefulness of the workman. Buff split leather is seldom embossed. To imitate the odor of morocco leather, oil of birch or cade is added to the pyroxylin solution before the latter is applied to the leather.

**Coating of Grain Splits.** This is the most valuable part or "heart" of the leather, and its value depends in a great measure on the depth of the buff and flesh coats which are split off. It is evident that a thinner buff and flesh split results in a thicker and more valuable grain split. In the coating process the hides are first soaked in order to render them as pliable as possible, the skins being naturally shrunken from the astringent tanning and chrome liquors through which they have passed. As coated leathers are always sold by the square foot, the skins are soaked and nailed to frames, being stretched out all that is possible in order to obtain the maximum area. They are fastened to wooden frames with large tacks, where they are allowed to remain until thoroughly dry, when the tacks can be removed without the leather shrinking. This process is called "drying to get the measurement." Although a thicker and more dense hide will require a longer time to dry than a thin, porous one, the degree of dryness is determined by the "feel," and after the hides have been removed from the frames they are preferably kept in a warm, dry room to minimize subsequent absorption of moisture. It has been found that a dry hide coats more readily and the coating composition adheres more firmly than if the leather has been previously exposed to a damp atmosphere for any great length of time. Irrespective of the manner in which the skins

have been tanned they are usually coated in the same way, variations being made for the weight and porosity of the leather at the time the composition is applied. A hide is laid on a low flat table, preferably glass covered, and the prime or first coat applied, usually with a 2-inch brush with bristles 6 inches long. The pyroxylin solution is uniformly and thoroughly worked into the leather substance with the brush, until apparently no more will be taken up. In some instances the dust from the splitting process is removed from the leather and the surface roughened by a stiff brushing before coating, in order to produce a firmer anchorage for the coating fluid. Where the finished leather is intended for fine upholstery, hand bags, automobile trimmings and carriage-tops, castor oil and not linseed oil is used, the formula for a first-coat composition being:

Pyroxylin .....	8 oz.
Commercial wood alcohol, 97% .....	45 fl. oz.
Amyl acetate .....	20 "
Refined fusel oil .....	12 "
Castor oil .....	12 "
Benzine 71°, sufficient to make 1 gal.	

The pyroxylin is first mixed with the amyl acetate, and the wood alcohol with the castor oil. The two are combined and the fusel oil finally added in small portions at a time with much stirring. Any pigments introduced are first ground in a small amount of the castor oil. After the application of the first coat the skins are hung on frames over steam pipes, the temperature of which does not rise above 40°, where they remain until dry, usually about two hours. They are again placed on the table and all "knots" and "warbles" polished off by smoothing the leather with pumice-stone. Warbles are excrescences on leather caused by the deposition of the egg of the gadfly in the hide of the living animal and the purulent abscess which forms upon the hatching of the larva. The second coat is similarly applied, but the above solution—less the castor oil—is mixed in equal volumes with the formula above, i.e., the amount of castor oil is halved. More care is exercised in uniformly and thoroughly covering the skin, and it is left on the coating table until dry to the touch. Then the skin is placed on a frame and the remainder of the solvent carefully expelled at a low temperature. The large proportion of low-boiling solvent in the formulas renders it impossible to apply the composition with the slicker, for the evaporation would be too fast to enable a proper spreading before the coat becomes hardened. The third and final coat,

consisting of the formula above but with no castor oil, is thinned usually about one-half, and allowed to flow out and over the skin and to dry at ordinary temperature until "set." After a thorough final drying, the skin is ready for embossing. A plate embosser, similar to that described in Chapter XI is used, the temperature of the steam chest being kept close to 70°. The leather is then considered finished, or if an extremely glossy appearance is desired, the hide is hung up and a weak (2-3 oz. per gal.) pyroxylin solution, in commercial wood alcohol and acetone only, sprayed lightly over the surface with an atomizer. The light boiling-point solvent allows of evaporation before the composition begins to flow or "run." If a "dead" or "mat" appearance is required, a pigment ground in fusel oil, and thinned with acetone, is sprayed on the leather in a similar manner. The volume of the spray is too small to affect the appearance of the graining.

In the process for coating grain splits as developed by S. Pianko and M. Knaster<sup>2</sup> castor oil and celluloid in solution are recommended, but experience has shown that the presence of camphor is entirely unnecessary. Leon Feval<sup>3</sup> recommends the use of so large an amount of castor oil in the first coat "that the inner coat or coatings will never entirely dry, and always remain in a 'tacky' or sticky condition." He makes the outer coatings sufficiently thick so that upon drying the outer will sufficiently protect the inner coatings. The process he describes as follows:

"The uncoated leather is first coated with a liquid containing the oil and nitrocellulose in solution and preferably diluted with alcohol with or without other materials, such as gums or pigments. This inner coating is allowed to set, (preferably at ordinary temperature.) The first or inner coating when sufficiently set will not be entirely hard and inflexible, owing to the presence of the large proportion of non-drying oil, but, on the contrary, will be tacky and more or less soft, flexible, and elastic. A second coating is then superposed upon it. This outer coating may be like the inner one except that it has a smaller proportion of the oil than in the inner coating. In this outer coating a larger proportion of pigment is used. The outer coating in some instances may contain no oil whatever, the effect of the oil in the outer coating being secured by the combination of the nitrocellulose of the outer coating with a portion of the oil of the inner coating. The idea of the outer coating is to serve as a finish to the inner coating,

1. If there is any tendency of the oil to remain on the surface due to the combined heat and pressure of the embosser, a piece of paper interposed between the embossing plate and leather will absorb any stains.

2. E.P. 28743, 1907; F.P. 385900, 1908; First Addition Mar. 9, 1908.

3. U.S.P. 848357, 1907.

the latter being always soft, and therefore impractical for a finished leather. If desired, a third or other coatings may be added, similar to the second. The process may be modified by making the second or additional coatings similar to the first.

"As an example for carrying out this process the following proportions may be employed: For a steerhide split or cowhide split of average thickness for the first coating a solution of about 13 lb. of pyroxylin dissolved in about 13 gal. of a mixture of 3 parts of wood alcohol and 1 part of amyl acetate. To this is added about 75 lb. of castor oil together with about 2 lb. of any commercial pigment, depending upon the color desired, ground in about 20 lb. of oil. The oil will therefore be at the rate of about  $7\frac{1}{3}$  lb. to each pound of nitrocellulose. The inner coating will set and will not permeate the leather to any appreciable extent. One reason why this is possible is the use of the wood alcohol in large quantity, so that the composition will not entirely or much of it permeate the leather and change the character of the coating from one of great elasticity and ability to stretch to a film formed largely of pyroxylin and incapable of being stretched. For the second coating the same amount of pyroxylin and amyl acetate is used, but with a smaller proportion of alcohol, depending upon the weather during the operation—on account of its tendency to absorb moisture and then precipitate pyroxylin. To this is added 16 lb. of castor oil.

"The amount of alcohol used in the second coating depends upon the weather during the operation. The second coating is in a position to absorb moisture, while the first coating is covered. Therefore if moisture be absorbed a spotted appearance in the coating results. It is possible to make it without alcohol; but the solution will penetrate too far unless other means be provided to prevent this, for the reason that the amyl acetate dries too slowly. The amount of oil in the inner coating is regulated by the thickness, texture, stiffness, and in some cases by the method of tannage of the leather, and also by the length of fiber on the surface, if the leather is a split. A thick and close-textured leather will require a larger proportion of oil than a thinner leather or one in which the texture is more open. In some instances chrome-tanned leather will require a smaller proportion of oil than a bark-tanned leather. The hand-buffed and machine-buffed leathers will require a smaller proportion of oil than the split referred to above, assuming the proportions to be the same in both cases. The proportions of oil to nitrocellulose should be varied when used in connection with other leathers—such as goatskin, calfskin, etc.—according to the above rule. The proportion may vary from  $7\frac{1}{3}$  lb. of oil to each

pound of nitrocellulose or even slightly more in some leathers down to very much less in other leathers. It may not well be reduced below  $3\frac{1}{4}$  lb. to each pound of nitrocellulose. This proportion of oil, it is to be understood, is to be measured by the amount of nitrocellulose employed and does not in any way depend upon the amount of solution containing the nitrocellulose. The proportion of oil in the outer coating will vary according to the results desired. A smaller proportion of oil will give a leather having a "drier feel." Similarly a larger proportion of oil will give an increased sleekness of feel. The amount of pigment added should be sufficient to secure the desired depth of color, the proportions used varying with the results desired. The addition of gums or other oils cause a slight reduction of non-drying oil. For instance, if a substance, such as camphor is used, and which is soluble in the solvent used to dissolve the pyroxylin without acting on the pyroxylin, it would be in the proportion of about  $\frac{3}{4}$  lb. to each pound of castor oil used. After the leather is coated it may be further finished by graining, embossing, or pebbling in the usual way.

"By microscopical examination of a section of leather coated by this process the different coats may be identified if they have been applied at an interval of two or three days between each, the coats containing the large proportion of oil showing in section a heavier or thicker coat of a peculiar gelatinous appearance."

**Coating of Flesh Splits.** These, being quite porous and not very strong, are used after coating for cheap upholstery, carriage trimmings and similar purposes. Heavier coating compositions are used on account of increased porosity of the leather fiber, but otherwise the coating is essentially the same and is applied to the outer or grain side. The light and fancy colors are seldom used with this class of leather, and only brown and black shades.

M. Pianko<sup>1</sup> attempts to produce the equal of the more expensive grain-split coated leathers by a rational and apparently satisfactory process in which the least expensive flesh split is attached by means of pyroxylin to a coated thin buff split, thus giving the weight and appearance of grain-split leather. This ingenious method consists in securing the desired pliability by first coating the flesh leather with a linseed oil composition containing sufficient pyroxylin to readily combine the surface with a pyroxylin cement. A light buff-split leather is then lightly coated with a pyroxylin composition high in nitrocotton, and either free from or containing just sufficient linseed oil to impart a high gloss. Flesh splits of the cheapest hides may be

1. E.P. 9304, 1902.

thus cemented to the buff splits of the more expensive ones. This method allows of much amplification and apparently opens up possibilities for the preparation of leathers of any desired qualities by combining, say, a porous split flesh, with a hard buff split, a leather of nearly the value of a grain split being thus produced, and at a fraction of the former cost. This suggests the possible solution of the problem of artificial patent-leather formation, except instead of applying the coating directly on cloth, the thinnest buff splits are attached to the cloth and the whole finished as with grain leather. The various processes of "boarding" and "pebbling" could be applied to a cloth surface cemented with a split leather, and the whole be then embossed in the usual manner.

**Chrome-Tan Leather.** There is but little difference in treatment of chrome-tan as distinguished from bark-tan leather, so far as coating is concerned. Chrome-tanned leather is less porous, more firm and less receptive to fluids than the same skin tanned with tannin. Therefore in general chrome-tan leathers require pyroxylin preparations of greater fluidity in order to obtain the desired result. If enameled or patent leather is to be made from a chrome-tan skin, especial attention must be paid to the dyeing of the skin black, as the dyestuffs penetrate the leather very slowly. In the two-bath chroming process, it is essential that the fat be removed from the skins as much as possible, and this is done either by hydraulic pressure or by extraction of the fat with benzene or other solvent. The hair is removed by de-liming, then bathed as in tanning, washed for a few minutes in a weak lactic acid bath, and if the skins are not sufficiently purified, a final washing in a weak, warm borax solution follows. Usually the skins are plumped by immersion in a "pickling" solution of dilute acetic or hydrochloric acid, containing from 3-10% of salt. The first bath of the process consists in adding to the pickling solution the required amount of potassium bichromate or sodium bichromate dissolved in hot water the hydrochloric acid already present increasing the penetration of the bichromate. The skins and solution are placed in a revolving cylinder and turned or "drummed" for a sufficiently long period and until the center of the heaviest hide shows a uniform green color. The skins are then removed and allowed to drain for from 6-18 hours to equalize the penetration of the chromic acid, the skins being kept excluded from the light to guard against reduction of the bichromate. After this they are washed free from bichromate, dried and finished in the usual manner.

The second bath of the process consists in reducing the bichromate to chromic oxide, usually by an acidified solution of sodium hypo-



sulphite (thiosulphate), the skins being dipped singly into the reducing bath, or a number are placed in a vat and agitated, the solution in this instance being weaker, and the time of agitation increased. Often 5% of commercial hydrochloric acid calculated on the weight of the skins is added to the vat liquor, the addition of the acid changing the color of the latter to a milky white color. The skins first become yellow, but finally assume a bluish-green color, and lose the slippery rawhide feel as they become changed into leather. They are finally carefully washed and dried after stretching on frames.

In the "one-bath" process, the oxidation with chromium and reduction of the same is carried out in a single operation, and "chromion," "tanolin," "vulcanochrome," "corin," "chromatin" and "bichrone" are trade names for solutions of this nature. A solution of chromic chloride is prepared by dissolving chromic oxide in commercial hydrochloric acid, which is then partially neutralized with sodium carbonate, the resulting liquor consisting essentially of normal and basic chromic chloride, sodium chloride and a small amount of free hydrochloric acid. The salt serves a useful purpose in preventing the drawing or contraction of the fibers during the chroming process. The partial reduction of the chromium in the basic state, it is claimed, makes subsequent reduction unnecessary; simple immersion of the skins in the bath the required length of time to insure thorough penetration and subsequent washing, constituting the process. It is claimed that the free chromic acid produced in an acidified bichromate solution such as is used in the two-bath process weakens the leather fiber, and the smell of sulphur dioxide from reduction of the thiosulphate in the two-bath process is not only disagreeable to the workmen, but destructive to the leather as well. Eitner has also made some preparations, "cromul," "cromar," and "cromast," containing organic matter intended to modify the action of the chromic acid.

A large and growing trade in white chrome leather coated with pyroxylin has developed as the result of the following method of procedure. By treatment of chrome-tan leather after separation into the usual three splits with dilute oxalic acid in the presence of sulphuric acid, the light-green color of the leather is changed to a very light fawn—almost white. By pressing out the sulphuric acid and oxalic acid hydraulically, and immediately afterwards immersing the skins in a bath containing calcium carbonate in suspension, which is being rapidly stirred in order to prevent settling of the carbonate, the latter penetrates the skin, combines with the sulphuric and oxalic acids, forming white precipitates of the oxalates and sulphates of calcium in the interstices of the fiber, and gives to the leather a per-

manent white color throughout. The carbon dioxide evolved as the result of the interaction opens the "pores" of the leather and makes the subsequent penetration of a pyroxylin solution much less difficult. After complete union of the calcium and acid, the leather is taken out of the bath, washed until neutral, stretched on frames and dried. When dry, the superfluous oxalate and sulphate is dusted from the leather surface, when it is found that the entire leather substance is of a pure white color. By smoothing this surface with pumice, and applying a 6-8 oz. pyroxylin solution containing a small amount of castor oil to increase the pliability, a glossy white leather results, of great strength and suppleness. Before the above process was evolved it was customary to take the light-green chrome-tan leather, and coat it with a pyroxylin composition containing a white pigment in suspension. It was found, however, that so many coats were required to completely cover the green shade, that the film of pyroxylin and pigment combined was so thick as to crack with great ease, and if the number of pyroxylin coats was decreased, the covering power was correspondingly diminished so that the green color of the chrome would often show through the superposed opaque white coats. Infants' white shoes and the other uses of white leathers except ladies' gloves, have been fields in which this class of coated leather has found a ready use. As might be inferred, the wearing qualities of leather coated with pyroxylin free from pigment are much superior to that in which the white color is applied with the pyroxylin, due to the general fact that any inorganic solid in a pyroxylin coating composition rapidly reduces its adhesiveness and tensile strength.

**Preparation of Patent and Enameled Leather.** Until quite recently, the great bulk of the enameled and patent leather produced for the market was still manufactured by the original process of using boiled linseed oil in the several coatings, the first coat containing a pigment to impart the desired color, the final coats consisting of linseed oil prepared with driers to form a readily flowing and gloss-giving varnish. The process is slow and laborious, for between each coat, the surface is smoothed or "pummied" by polishing with a piece of pumice stone. The coatings were exposed outdoors to sun and dust to complete the drying process, and even with the utmost care a great many sides of leather when finished were of but second quality by reason of defects in the finished article.

The advantages of pyroxylin coating as compared with the above, are ease and facility of manipulation; elimination of "sunning" and exposure to dust, the absence of sunlight for a period not impeding the process; drying at a low temperature which can be readily con-

trolled; and the production of a gloss and luster on a hard surface and one in which the coefficient of expansion is low, so that the greatest defect in patent leather—that of cracking on exposure to sudden changes in temperature—is in a great measure obviated when the coating is properly conducted. It is customary to dye the leather black before coating.

The process of coating leather with nitrocellulose is comprised in the following three distinct steps: (1) boiling the linseed oil; (2) preparing the pyroxylin solution and incorporating it with the oil; and (3) the actual coating and finishing of the leather. A complete process is herewith outlined in which the latest methods and the reasons therefor are given, and which may be considered as fairly representative of the most successful present-day methods.

**Boiling the Linseed Oil.**<sup>1</sup> A convenient quantity of oil, say 100 gal., is placed in an iron oil-boiling kettle mounted on wheels and run on a track so that the kettle and contents may be run on and off the fire, coke or wood charcoal being preferably used as fuel. An oil-boiling thermometer is attached to the inside of the kettle, which should not be over half filled with oil. After the fire has been started, the temperature of the oil has arisen above 100° and frothing due to escape of moisture in the shape of steam has subsided, the driers, previously mixed in a portion of the oil some hours before, is added in small portions and thoroughly stirred in.<sup>2</sup> One-half oz. raw umber and  $\frac{3}{4}$  oz. Chi-

1. The essential point in boiling linseed oil for this and similar purposes is to keep the heat sufficiently low so as to start no destructive distillation to "crack" the oil, but simply sufficient heat to induce polymerization of the glycerol esters of the oleic, linoleic, linolenic and isolinolenic acids present, and induce the formation of metallic oxide combinations with the unsaturated acids above named. If the temperature is kept moderately low, and the oil is constantly stirred to eliminate the decomposition products of glycerol, as acrolein, the polymerization of the unsaturated fatty acids is accelerated with the formation of complex substances which more rapidly absorb oxygen. The nature of the dryer added appears to be of less moment than the proper combination of that drier with the fatty acids present. On storing linseed oil, the moisture and mucilaginous matters gradually subside, certain oxidation processes are carried on in the oil, and it thereby acquires a higher value, especially in the preparation of varnish similar to the above. Such oil, often kept for years, is called "tanked" oil, and its suitability for pyroxylin combination is determined, in a measure, by heating the oil in a test tube, when no mucilaginous matter should separate and the oil should remain clear. This "mucilage" consists of pectinous products, phosphates and sulphates (G. Thompson, J.S.C.I., 1903, 22, 1005). To facilitate settling, the oil may be refined by treatment with 1-3% sulphuric acid, when a charred mass forms which subsides and takes with it the bulk of the impurities. The refining processes by treatment with ozone apparently have not been successful. In resplendency and elasticity of film, it is the general opinion that oil settled and clarified by time makes the most satisfactory coating compositions. See "Linseed Oil Boiling for Enameled Leather." G. S. Wolf, U.S.P. 632163, 1899.

2. In the proportions named, the driers apparently go entirely into solution. Lead has been found unsuitable, as oil boiled with litharge or other lead compound is prone to crack, perhaps from a continuation of the oxidation process after being

nese blue, per gal. will give satisfactory results.<sup>1</sup> The heat is continued, stirring preferably being continuous, the increase in temperature being at the rate of about 10° each 15 minutes until a maximum of 275° has been reached. The oil by this time will usually be of the consistency of thick molasses;<sup>2</sup> if not, heating is continued, always with continued stirring, and in order that the temperature may not rise above 275° the oil is taken off the fire and stirred until the temperature has been reduced a few degrees. These successive "heats," as they are termed, are continued until the proper viscosity is obtained. The kettle and contents are then removed from the fire, covered and left at rest until the temperature has fallen to 100°, when 20% (by volume of original oil taken) of amyl acetate is added at once,<sup>3</sup> and thoroughly incorporated with the oil. The cover is again replaced and the contents left to cool to atmospheric temperature, when it is removed and filtered through a paper filter in a plate-filter press, after which a sample of the oil-amyl acetate when placed on a sheet of glass and interposed between the observer's eye and sunlight, should show an entire absence of solid particles or granulations. The mixture is then tanked until ready for use.

**Preparing the Pyroxylin Solutions.** In general, the nitro-cotton—which, when dissolved 6 oz. to the gal. in amyl acetate 60 parts, benzine 40 parts, has a viscosity about like that of rape oil—is considered most suitable. There has been much investigation as to the best combination of solvents, the highest authorities agreeing that the amount of amyl alcohol (refined fusel oil) should not be far from 20–22%. But little wood alcohol and no acetone or ether are used.<sup>4</sup>

applied to the leather. Large amounts of driers are not only unnecessary, but harmful.

1. "Chinese blue" is a complex ferrie ferrocyanide of variable composition.
2. Corn, peanut, rape, hemp, and mustard-seed oils all appear to be inferior to linseed for this purpose. Chinese or Japanese wood oil, although probably the most readily oxidizable oil known, is of no value in pyroxylin coating compositions, for in boiling, if the temperature of 125° is reached in the boiling process, the oil may suddenly solidify in the kettle. See process of W. Blakeman, U.S.P. 767682, 1904.
3. The acetate should be added quickly and stirred thoroughly so as to cool the mass as soon as possible and thus minimize evaporation of amyl acetate. If the oil is left until cold before the addition of acetate, the mixture may appear slightly granular even after filtration, whereas when added hot, a perfectly homogeneous liquid will result. The tests usually applied are to take a small portion of the oil from the kettle on a spatula, and testing its "stringing" qualities between the thumb and first finger. In some works 5–10% of the amyl acetate is substituted by turpentine.
4. All on account of rapid evaporation due to low boiling point. A successful coating composition must be sufficiently slow in evaporating so that when applied to a large skin the operator will have sufficient time to thoroughly and properly cover the skin before the solution has evaporated to such a consistency as to make spreading difficult from the tendency of the composition to "rub up." This is a most important point in the preparation of this class of pyroxylin solutions.

Benzine 62° Bé. is preferable to the lower boiling 71° Bé. fraction. The amyl acetate should be preferably rectified and the higher boiling-point fraction used, and this should be practically free from propyl acetates.<sup>1</sup> The dyestuff is one of the modern spirit-soluble nigrosines of the highest concentration, and hence free from dextrin and appreciable amounts of salts. The dyestuff is filtered after first dissolving in a mixture of equal volumes of amyl acetate and benzine. A typical coating composition would possess about the following composition:

Pyroxylin. . . . .	8 oz.
Amyl alcohol . . . . .	26 fl. oz.
Amyl acetate . . . . .	70 "
Benzine 62° sufficient to make 1 U. S. gal.	

The amount of nigrosine required will depend upon the brand and strength of the dyestuff and the depth of shade required. The coating composition should be made up a few days before use<sup>2</sup> and preferably paper-filtered through a plate press.<sup>3</sup>

The oil (containing 20% amyl acetate) is mixed with the pyroxylin solution, by adding the latter to the former and not the reverse. The proportions vary with the different coats, being higher in oil with the first coat, and free from oil in the final coat, where a hard surface is desired. Satisfactory results have been obtained where the first coat consisted of 1 part oil mixture, 3 parts pyroxylin, and the second coat,

For the same reason the amyl acetate should be high boiling and reasonably free from lower acetates, and benzine 62° is preferable to 71°. No doubt, also, the fact that best results are obtained with a preparation high in amyl alcohol is due in a large measure to this fact, although the latter, it will be remembered, is an absolute non-solvent of nitrocotton. With solvents of high boiling-points as outlined above, when the usual amount of composition is spread over a large skin (about 3 ounces for a skin aggregating 15 square feet) the same can be manipulated and brushed in thoroughly without sufficient loss of solvent to make the lacquer difficult of brushing or spreading, or causing the composition to granulate and roll up on the leather.

1. Because American fusel oil is first water-washed and the lower alcohols thereby removed, American fusel oil acetate is of higher boiling-point than a similar product made from German and Russian oil, in which washing out of the lower alcohols is not compulsory. See Chapter VI.

2. When a pyroxylin solution is allowed to stand a few days the finer insoluble particles apparently combine into larger ones, for it is noticed that a freshly prepared solution does not filter as readily or clearly as one which has been allowed to stand.

3. Two points of importance in determining the suitability of a given pyroxylin solution for leather coating are freedom from "specks" (clearness) and miscibility. The former is of great importance because each speck means a "pinhole" or small excrescence in the leather when the coating is applied, these pinholes often being the weakest points in the leather and hence the place which breaks first in wear. Therefore, the solution should be subjected to paper filtration. The lack of satisfactory coating results undoubtedly are often due to overlooking this point.

1 to 6 respectively. It is considered better practice to mix oil and pyroxylin several days before use.<sup>1</sup>

**Applying the Compositions to the Leather.** The principal point to recognize in coating is the formation of a film at the same time flexible, yet hard and tough. These two as applied to leather coverings are entirely antagonistic, i.e., the tougher the coating the less flexible will it be, and conversely, any increase in the flexibility will be a decrease in the strength of the coating product. In coating leather for a definite use or purpose, it must be decided how much one will concede to the strength of the leather covering to obtain the greatest flexibility. The fact that a compound of pyroxylin is hard and bends with difficulty does not necessarily imply that flexibility and elasticity are thereby decreased. Admitting that the non-drying and some of the drying vegetable oils added to coating compositions lessen the strength and durability of the applied coating, it follows that the greater the amount of oil originally present in the leather, the greater will be the difficulty in obtaining a tough exterior coat. The condition of the leather before coating, therefore, is of extreme importance in obtaining uniform and satisfactory results. In applying any leather covering, the composition must first obtain a hold on the leather substance itself as a basis for the building up of successive coats into a satisfactory whole. If the first application does not adhere with the requisite firmness, it is evident that successive coats, while they may completely unite to the next preceding coat, yet the whole coating may come off *en masse*, due to defective adhesion of the primary layer. Therefore the first and most important point in pyroxylin leather coating is the formation of a sufficiently firm foundation, as a nucleus upon which successive layers may be built. It is also of great importance that each coat should be thoroughly dried before the next is spread upon it, else the new solvent will cut through into the under coats, and pull them from their anchorage, the result being a loosening of the entire coating layers or the formation of "pinholes" due to uneven evaporation of solvent.

1. To judge whether the mixture is perfectly homogeneous, a small amount is allowed to run off from a glass plate and the plate interposed between the observer and the light. If the oil and pyroxylin have not combined properly, the mass will appear slightly granular. No specks should be visible to the naked eye. If such can be detected the oil-pyroxylin mixture should be paper-filtered. It is unnecessary to state that these solutions must be carefully protected from dust. It is stated to be a common practice when the oil and pyroxylin solution go together with difficulty, to add a small amount of acetic or nitric acid (not over 0.5%) and stir vigorously, when the oil-pyroxylin mixture will often lose its granular appearance and become homogeneous. The reason for this is not apparent to the writer, and the free acid must materially decrease the viscosity of the mixture, if the latter is allowed to stand for any great length of time before use.

The leather is first soaked, tightly stretched on frames by tacking until dry and with the skins still on the frame then placed one at a time on tables preferably covered with glass. The hide is carefully smoothed out and thoroughly and vigorously brushed in order to remove any dust or extraneous particles which might interfere with the smoothness of the coating or the firmness of its attachment. The brushing also superficially roughens the surface and presents a better surface for adhesion. A small amount of the oil-pyroxylin solution which has been warmed to 30–32° is taken up on the side of a blunt knife called a "slicker," the amount depending on the adroitness of the workman to thoroughly incorporate the mixture in the hide before evaporation is carried to a point when the pyroxylin begins to precipitate out. The mixture is thoroughly and evenly rubbed in the hide surface until apparently no more can be assimilated. This amount will vary within wide limits, depending on the size and receptive nature of the hide.<sup>1</sup> A brush is not suitable for applying this coating, as the penetration cannot be as thoroughly carried out when brushed as when actually rubbed in. After partially drying on the table, the hide (still fastened in the frame) is placed over steam pipes in a frame, the temperature of which does not rise above 35° and left to dry usually for 24 hours. The surface is then lightly smoothed with pumice stone in order to "polish off the nap," before the second coating is applied.<sup>2</sup> This coating, as stated, contains about half the amount of oil of the first coat, the solution being brushed on with long bristle brushes, less often with a sponge. Wherever places appear in the hide which seem to have been coated too lightly in the first operation or which were pumiced off too closely, a larger amount of coating material is applied, a primary object of the second coat being the formation of a uniform, smooth base upon which the final coat may be flowed. The leather is allowed to remain on the table until the coating has "set," when it is "ovened" or dried as before. This coating is not to be considered as sufficiently dried if a smell of solvent can be detected when the film is peeled off with a blunt instrument. In some methods, two intermediate coats are given, being spread on quite thinly, but if the first coating has been properly applied and the resulting surface uniformly smoothed, the second coat when dry will present a smoothness such that when the final coat is brushed over, and dried, the surface produced when viewed by reflected light will be entirely devoid of undulations or solid particles. In enamel

1. The more porous the hide, the less fluid and heavier the pyroxylin solution applied, and conversely.

2. Visual examination of a hide is the best criterion of the amount of coating solution to be applied, which skill comes only by experience.

leather the final coat is usually pyroxylin without oil, while in patent leather, where the highest gloss is desired, a small amount of linseed oil is added to the pyroxylin solution. This last coat should be quite thin, and contain sufficiently high boiling-point solvents, so that when applied to the leather surface the final coating will admit of repeated brushing without showing the brush marks, and will ultimately flow out to a highly glossed even surface. On the other hand, the final coat must, however, be applied with such dispatch that the former coats are not sufficiently softened by the solvent so as to rub up in the brushing-out process. After a final drying, still at reduced temperature, the leather is taken out of the frame, and if not quite flexible enough a coating of linseed or castor oil may be given the under side of the hide.<sup>1</sup> The finished leather should not be cut and worked up before a week after coating, to give plenty of time for the last traces of solvent to evaporate and the coating to assume the maximum hardness. This process with properly tanned hides and due attention to details results in the formation of patent and enamel leather which should fully withstand the rigorous requirements of the trade. "Linseen," "cellulone" and "patentoid" are trade names for linseed oil-pyroxylin leather-coating compositions.

**Production of Colored and Fancy Coatings.** The color, a dyestuff<sup>2</sup> (preferably), or a lake, is added to the inner coating compositions. Wherever possible the leather is dyed the color desired, so that the coating material may be free from dyestuff or pigment, both of which, especially the latter, materially weaken the pyroxylin film. The lake or pigment is first ground in a small amount of the vegetable oil used, or if a dye, is dissolved in wood alcohol and amyl acetate and filtered before use. Otherwise the coating processes are the same as previously described. The coating operations for goat, calf, sheep, and various other hides do not materially differ from the descriptions given above, any variations depending rather on the thickness of the leather and its compactness due to the tanning or chroming processes, rather than to the origin of the pelt.

1. Or the under side of the coated skin may be slightly "fat liquored" by lubrication of the fibers with dégras or other oil.

2. Among the single acid dyestuffs suitable for dyeing vegetable-tanned leather are, azo yellow, phosphine, chrysoine, Indian yellow R., naphthol yellow S., Cuba yellow, turmeric yellow, fast acid yellow for yellows; solid-, acid-, fast-, resorcin-, dark nut-, and acid-browns, mikado brown B., for browns; scarlet R., crocein scarlet 3 BN., orange 2, mandarin G., bordeaux G., atlas orange, and fast red A., for reds and oranges; guinea-, acid- and light-green, and erioglaurine for greens; acid- and formyl violet; Bavarian-, marine-, and solid-blue; among the basic dyestuffs are: chrysoidin, vesuvin, rheonine, and bismarek brown; auramine xanthine, canella, coriphosphine, paraphosphine and acridine yellow; methyl, methylene, solid and malachite greens; safranine, fuchsine, rhoduline and Russian red and the methyl and crystal violets.



**The Coating of Furs and Skins.** The unusually heavy demands made on the fur industries for coats and cloaks, mainly attributable to the rapid rise in the use of the automobile, has brought out a process for the treatment of the flesh side of tanned furs in order to increase their warmth. This consists in treating the fur with a plurality of pyroxylin coats, the number and nature of the coatings depending somewhat upon the source of the fur and its relative cost. Ordinarily four pyroxylin coats are applied to the fur after tanning. If the garment is to consist of but few pelts or pieces, the cold-proofing is best done on the skin in the raw state, that is, before being worked up into the garment. If, on the other hand, however, the garment is to be composed of many pieces sewed together, best results are obtained by applying the coatings to the finished garment, that the thread holes and places where two pieces are sewed together may be filled with the pyroxylin as well. In both instances the solutions and number of applications are the same. If the pelt as a whole is to be coated, it is spread over a hard smooth surface, usually a glass-covered table, and a coating mixture high in castor oil first applied of a composition somewhat as follows:

Castor oil.....	16 oz.
Pyroxylin.....	8 "
Commercial wood alcohol, 97 $\frac{0}{100}$ .....	30 "
Amyl acetate.....	30 "
Refined fusel oil.....	25 "
Benzine 62° sufficient to make 1 gal.	

The pelt is usually first thoroughly moistened with a mixture of equal volumes of wood alcohol and amyl acetate, to make the skin more receptive to the pyroxylin and induce deeper penetration of the fluid. While still moist, the first coating is applied with a stiff brush and thoroughly worked in, until apparently no more will be taken up by the skin substance. Then a heavy coating is placed on the inner side of the fur, and the whole allowed to dry at ordinary temperatures in a fairly dry room, which requires from 24 hours upward. Drying is completed at a temperature not exceeding 50°. It is very essential that this coating be thoroughly dry before the next one is applied, that the subsequent coat may not too deeply cut into the prior one. In order that the coating composition may be insecticidal, naphthalin, camphor, salicylic, benzoic and cinnamic acids and other insect-repellant chemicals may be dissolved in the wood alcohol used in the coating composition. The use of naphthol and naphthalin has to be

guarded against, for these often affect the shades of the dyestuffs with which the fur has been colored. The second and subsequent coats are substantially alike, and differ from the first or "prime" coat in being entirely free from oil. They are applied in a similar manner. It is said that by means of this pyroxylin coating process, but little additional weight is added to the skin, while the warmth of the garment is increased very materially, and the life of the skin in many instances greatly prolonged.

To improve the wearing qualities of tanned boa constrictor and other serpent skins and the skins of certain fish as the shark, all of which find ready sale, they are preserved from wear and a gloss is imparted to the skin, by coating both sides with a 5-6 oz. pyroxylin solution containing from  $\frac{1}{4}$ - $\frac{1}{2}$  oz. arsenious oxide per gal. of solution to guard against the ravages of insects. When arsenic forms an ingredient of the coating mixture, it is usual to dip the skin in a final solution of pyroxylin containing no antiseptic. Ornaments and reticules made of skin thus prepared can be cleaned by washing with soap and warm water.

## CHAPTER XIII

### ARTIFICIAL FILAMENTS

Of all the textile fibers, silks are the simplest in structure, most perfect, and most highly prized. This undoubtedly accounts for the fact that the silk industry is one in which production has never been in excess of a constantly increasing demand. It is therefore quite natural that with a subject so alluring financially, many early endeavors were made to prepare substitutes which would possess in a high degree the desirable properties of luster, elasticity, and strength, properties so highly prized in natural silk. It was reasoned that the silk fiber, being devoid of cellular structure and consisting primarily of the solidified liquid contents of the glands of the silk worm,<sup>1</sup> would be apt to offer a much more inviting and remunerative field for speculation and experiment in attempting to imitate it artificially, than would the more highly organized fibers of cotton or wool.

It would only be necessary, it was reasoned, to project an acceptable liquid of known viscosity and total solids through orifices of a desired diameter, and thus form filaments which, like those of natural silk, must be insoluble in water and of sufficient strength and elasticity

1. Of other artificial filaments may be mentioned spun glass, which may be formed by rapidly drawing out a glass rod heated until soft. As spun glass may be prepared from colored glass, the product may and has been used for the production of colored fabrics. Dresses made entirely of spun glass were exhibited at the Columbian Exposition of 1893. In consequence of the low elasticity of glass, the commercial value of textiles so produced is practically *nil*. Such fabrics rapidly become disintegrated on account of the brittleness of the fiber, the minute particles of glass which are continually separated from such fabrics being highly injurious when inhaled. The curly glass wool used for filtering purposes is produced by drawing out two glass rods of unequal hardness to a double capillary thread. On cooling these curl up on account of their different coefficient of expansion. From very early times silver, gold and other threads have been used in the decoration of royal fabrics. The so-called Cyprian gold thread, famed for its beauty and permanence in the Middle Ages, is now produced by covering flax or hemp with gold foil. When molten slag is projected against a steam blast, the slag is blown into a very fine fiber, used as a packing material and for insulating and fireproofing purposes. Asbestos is probably the best known of the mineral fibers, being a double magnesium calcium silicate containing iron and aluminum. Asbestos fibers are difficult to spin in themselves, but when mixed with cotton it is readily woven into fabrics, the cotton being removed by afterwards heating the fabric to incandescence. Asbestos is difficult to dye, the albumen and substantive dye-stuffs being most applicable.

to admit of spinning and weaving without serious deterioration. The entire problem is comprised in the foregoing sentence, and as yet it has not been solved in two particulars, viz., a solution has not been found which would immediately set to a fiber of the required strength when a liquid is projected into the air as it occurs in nature, all efforts so far having had to rely on liquids to coagulate or set the thread. Secondly, from a chemical standpoint, the fluid present in the gland of the silkworm differs only from spun silk apparently in being a liquid, because as soon as it is artificially removed for purposes of analysis, it becomes hard and identical with the spun filament. Much research has been expended—as yet without material success—on the subject of utilizing silk waste and noils by converting them into a solution without altering their chemical nature or physical deportment, and work with them along methods similar to those used with collodion solutions. The mechanical portion of the problem appeared to be merely the formation of threads by forcing the liquid through the orifices into the coagulating or solidifying media, air being the least expensive and most readily obtainable. Up to the present time, however, all the artificial silks produced have been lacking in flexibility and strength, and their present increasing popularity, and hence consumption, are mainly dependent upon the fact that in luster and appearance they equal, if not exceed, that of the natural product. It is probable that the extreme brilliancy and softness in feel are the two factors which prolonged interest in the artificial product, until sufficient research in other directions led to improvements which gradually eliminated or decreased the other objectionable features, and caused such a demand for the yarn in comparison with the possible supply, that the price of the artificial silk for a time actually exceeded that of the real material.

The rise and development of the artificial-silk industry are an enumeration of difficulties overcome and ingenuity displayed in formulating ways and means whereby some form of cellulose, usually cotton, may be formed into a fluid and attenuated into merchantable filaments, and strikingly exemplifies the fact that man has learned to apply practically the lessons taught by Nature. It was Réaumur who in 1731 first explained intelligently the methods of the silk-worm in forming silk, and conceived the idea of accomplishing the same result artificially. Réaumur showed that silk was the product of certain glands located on the under side of the body of the silk-worm, and that a portion of the albumen of the silk-worm's food is transformed into fibroin and secreted in the glands. It therefore was quite **natural** that he should have propounded the question whether it

would not be possible and practicable to spin other semifluid materials, such as, for example, certain varieties of pitch, into thin filaments and thus produce a silk-like substance equally as serviceable as the fibroin of the silk-worm. It appears that Réaumur's time was undoubtedly ripe for theoretical discussion and speculation, but it was not ripe for the purpose of overcoming the technical difficulties presented, both chemical and mechanical. It was not until one hundred and fifty years had elapsed before sufficient combined experience had been accumulated to attack the problem in a successful manner.<sup>1</sup>

1. As stated in Sci. Am. Suppl., No. 1446, p. 23173, of a translation from Prometheus:

"Silk fiber is distinguished from all other fibers by the circumstance that it is not built up of cells, but constitutes a congealed fluid stream. This stream is produced by the silkworm, by discharging the contents of its glands through minute openings. As it comes into contact with the air the silky substance solidifies, thus producing a thread which can be continuously spun on until the gland is exhausted. The same result is to be produced by the means at our disposal, it would be necessary merely to discharge a suitable fluid from its containing receptacle through a very fine outlet. We should then reproduce the exact process carried out by the silkworm, and we should then form silk. But at this stage obstacles are encountered, which Réaumur, although he did not clearly recognize them, still suspected their existence. To use his own words: 'It will be impossible to produce as fine threads as are produced by the silkworm, but it should not be impossible to spin out varnishes into threads of sufficient fineness.' In this statement the great technical difficulties of the problem are clearly indicated.

"That a fluid stream can be congealed can hardly be doubted; but the task consists in ejecting a stream of sufficiently small diameter. A stream is produced because every fluid has a definite cohesion. But fluids are subjected to the laws of another force besides that of cohesion, and this force is the force of superficial tension, according to which every fluid constantly tends to assume the form that will most uniformly occupy space. This form is a globe. The greater the mass of the fluid, the greater will be the cohesion; the smaller the mass the greater will be the superficial tension. For this reason every fluid stream, which is nothing more nor less than a cylinder of infinite length, will tend to divide itself into drops, that is, into individual globules. The finer the stream, the greater will be the tendency to produce globules. When streams of extreme fineness are produced it is not possible to prevent the formation of globules. Careful observation of a stream of water emerging from a pipe will prove that, as the stream becomes finer, a ring-like furrow will be produced, which gradually approaches the pipe outlet and disappears in a drop.

"The superficial tension must overcome the cohesion, and the cohesion varies with different fluids. For this reason some fluids are particularly well adapted for the formation of drops. The resistance which a fluid opposes to the tendency to form drops is called its viscosity. Fluids which have a very low viscosity, such as ether, can hardly be made to form a connected stream. On the other hand, very viscous fluids are not easily separated into drops. It therefore follows, that it would not be possible to produce artificial silk from every congealable fluid; but that it would be necessary to employ a viscous fluid which, as it is ejected from a fine opening, will form a continuous stream.

"A beautiful example of the utilization of physical processes in producing artificial silk is offered by the manufacture of shot. Most metals in their molten condition, despite their high specific gravity, have a low viscosity. A stream of metal, therefore, is easily separated into individual drops which solidify as they cool off. Mercury is an admirable example of a metal of small viscosity but of enormous superficial tension. If molten lead be poured through a sieve rotated on top of a tower, the streams of fluid metal immediately separate into drops which are congealed and solidify before they reach the bottom. A large number of

The idea was resuscitated in 1885 by Andemars of Lausanne, who combined nitrated mulberry branches with rubber, and formed a solution which he drew out into a thread.<sup>1</sup> Apparently he considered that cellulose nitrate made from mulberry—the food of the silk-worm—must possess peculiarly desirable properties. Crookes, Weston,<sup>2</sup> Swan,<sup>3</sup> Swinburne,<sup>4</sup> and F. Wynne and L. Powell,<sup>5</sup> were the next to revive the subject of the use of nitrocellulose for artificial threads, which they did almost simultaneously in endeavors to produce electric light filaments by impregnating nitrocellulose with rare earth oxides, and who used respectively cellulose nitrates dissolved in glacial acetic acid, nitroglucose made plastic by heat, and cellulose dissolved in zinc chloride solution. All used alcohol to coagulate the formed thread. The commencement of artificial silk formation upon which the modern industries have arisen may be said to date back to 1881, when Count Hilaire de Chardonnet deposited a sealed document with the French Academy of Sciences, which, when opened on Nov. 7, 1887, bore the title "On an Artificial Textile Mate-

round balls of lead, in other words, shot, is the result. The opposite of that which occurs when lead and mercury streams are separated into drops must be accomplished by the fluid which is to yield artificial silk. In other words, the fluid must be viscous. But since viscous fluids flow slowly, and since superficial tension is overcome by causing the particles of the fluid to move forward in the given direction, it is not enough simply to press the fluid out of an opening in order to form streams of sufficient fineness. The superficial tension would simply lead to the formation of drops. This can be proved by pouring a solution of rubber, which is very viscous, into a vessel provided with a very small hole. Out of this hole there would emerge not a stream, the diameter of which would correspond with that of the hole, but thick drops which cling to the vessel. If the hole be fine enough, this drop may congeal through vaporization, thereby closing the hole and preventing the egress of further drops. A fluid of lower viscosity, such as water, would flow out of the vessel in a short time in a fine stream.

"In order to allow viscous fluids to flow out of the vessel in a fine stream, the pressure of the fluid must be in some way increased. This can be done by assisting the pressure with suction. If the drop of rubber had been touched with the finger at the moment when it was formed, and the finger then withdrawn, the rubber solution would have followed in the form of a fine thread. This is the process employed by the confectioner in spinning taffy or candy. And this is also the process employed by the silkworm in spinning silk. For the creature secures the first drop which emerges from the glands to some object, and assists the natural pressure of the substance by moving its head hither and thither."

1. E.P. 283, 1855. His process consisted of reducing the young branches of the mulberry tree to a paste, bleaching and purifying it, finally transforming the paste into an explosive substance (probably nitrocellulose), dissolving this substance in a mixture of alcohol and ether, then adding an ethereal solution of india-rubber previously treated with ammonia, and transforming the viscous liquor so obtained into a thread. The thread was spun by means of a simple point of steel, which was dipped into the mixture and then drawn out. This point drew out a viscous thread which rapidly dried, and which he then wound on a bobbin.

2. Electrician, 1887, 18, 287; E.P. 4458, 1882.

3. D.R.P. 161780; 1884; E.P. 3029, 1884.

4. Electrician, 1887, 18, 256.

5. E.P. 16805, 1885; abst. J.S.C.I., 1886, 5, 172.

rial Resembling Silk." His first patent<sup>1</sup> was taken out Nov. 17, 1884, and contained a description of the process of preparing nitrocellulose and squirting an ether-alcohol solution of it through minute apertures into the air. From this point the development of the four main branches of artificial filaments—nitrocellulose, cuprammonium cellulose, zinc chloride solutions and gelatin and similar materials, omitting viscose and cellulose acetate described separately—is perhaps more properly considered under their respective headings in a later portion of this chapter.

At first the idea appeared to be to produce an article as a direct competitor of natural silk, but with increased knowledge this is being gradually discarded. The lack of strength and wearing qualities of the artificial material have lessened liability to competition and replacement of the natural product, and instead has created channels of consumption of its own. In a great measure it has been the means of creating new uses for lustrous silk-like threads, e.g., for ladies' wear, trimmings, hats, and woven with silk and cotton in the production of mixed goods. Natural and artificial silk are more and more occupying distinctive fields, in which new industries are increasing for the use of the latter product. It is not exaggeration to say that the artificial-silk industry is creating an entirely new class of fabrics, which, except in a few cases, have not taken the place of natural silk at all. The general progress from the original highly inflammable films of Chardonnet to the denitrated and regenerated final cellulose filaments of the present time, and which resist the disintegrating action of water, have been achieved by very careful research and by distinct steps, as hereinafter enumerated.

The name "Artificial Silk" is rather a misnomer, for with the

1. F.P. 165349, 1884. For recent improvements in the manufacture of artificial silk see Wordle, *Text. Ztg.*, 1892, 53. *Ind. Text.*, 1892, 423; Hanaušek, *Chem. Zeit.*, 1894, 18, 441; Silbermann, *Mon. Text.*, 1894, 9, 51; Herzog, *Lehnes Farb. Ztg.*, 1894, 6, 49; Truchot, *Muster Ztg.*, 1897, 46, 535. *J. Pharm.*, 1897, 6, 400; *Mon. Teint.*, 1897, 41, 214; Levy and Ernst, *Lehnes Farb. Ztg.*, 1900, 11, 135; Pfeiffer, *Oest. Chem. Ztg.*, 1900, 3, 57; Suvern and Herzog, *Verh. V. Gew. Abh.*, 1903, 224; *Zeit. ang. Chem.*, 1903, 16, 600; *Rev. mat. col.*, 1903, 7, 269; *Ind. Text.*, 1903, 19, 69, 143; *Text. Mfr.*, 1903, 29, 209; Moss, *Ibid.*, p. 147; 1904, 30, 13; Witt, *Verh. v. Gew. Sitz. B.*, 1904, 71; *Lehnes Farb. Ztg.*, 1904, 15, 222; *Text. Mfr.*, 1904, 30, 99; *Farb. Ztg.*, 1904, 40, 688; Bellet, *Rev. ind.*, 1906, 37, 428; P. Hoffmann, *Ind. Text.*, 1906, 22, 1581; *Uhlands Trade Rep.*, 1906, 5, 28; *Text. Rec.*, 1906, 31, 5, 96; Wederhake, "Silver Caoutchouc Silk," *Pharm. Centrallh.*, 1906, 47, 862; W. Massot, *Zeit. ang. Chem.*, 1907, 20, 437; F. Beltzer, *Mon. Sci.*, 1907, 68, 181; C. Schwalbe, *Zeit. ang. Chem.*, 1908, 21, 2401; H. Silbermann, *Rev. gén. mat. color.*, 1908, 11, 186; A. Colin, *Rev. gén. Chim.*, 1909, 12, 40; J. Gilpin, *Am. Chem.*, J., 1910, 43, 469; H. de la Coud, *Rev. gén. sci.*, 1910, 21, 203. See also U. S. Daily Consular and Trade Reports, No. 3315, Apr. 20, 1908, p. 11; 3198, June 10, 1908, 16; 3350, Dec. 8, 1908, 7; 3431, Mar. 17, 1909, 10; 3488, May 22, 1909, 8; 3532, July, 15, 1909, 7; 3658, Dec. 11, 1909, 12.

exception of gelatin and casein silks, which have not reached any considerable degree of commercial success as yet, these artificial fibers differ from the natural in being of vegetable and not animal origin, as shown by their analysis and especially their behavior towards dyestuffs. Cross and Bevan have suggested the compatible name "Lustracellulose," J. Cain that of "Celvis," and O. Guttmann "Lustrose."<sup>1</sup> These names are intended to comprise artificial fibers as a class, irrespective of their composition. "Cellose," "Silkose," "Silkoid" and "Fibro-silk" have also been suggested. As in the expansion of any industry, all methods were not feasible and several companies were undoubtedly formed to work processes which had little chance of commercial prosperity.

A. Chaplet<sup>2</sup> has recently revived the subject of modern attempts to produce artificial tissues as entire pieces of fabrics without weaving. Millar, Drouinat, and others have attempted to produce such cloths directly, but as yet with but little commercial success.

**Nitrocellulose Silks** at the present time are easily the most important, both from the amount produced in comparison with the other methods and from the fact that it was the first filament prepared commercially in large amounts. The Chardonnet methods, with their modern refinements, are the most largely worked, the systems of Lehner and Du Vivier probably coming next in importance in the order named. Methods of solvent recovery admitting of a high percentage of solvent regenerated and which were apparently first perfected in 1909 and 1910, will undoubtedly exercise great influence in the expansion of the production of filaments with a cellulose nitrate base. The luster may be increased according to A. Palmer<sup>3</sup> by strongly compressing the moistened material at a high temperature, by passing it between heated cylinders at a speed sufficiently great to leave the material still wet after treatment.

As a class, the nitrocellulose silks dissolve in concentrated sulphuric acid and also in chromic acid; cold concentrated hydrochloric acid is without effect, but on applying heat the silk is speedily destroyed; with concentrated acetic acid the fiber rapidly swells up, as also in concentrated caustic alkalis and Schweitzer's reagent, but is not dissolved.

Iodine and sulphuric acid colors the silk a blue; Vetillard's reagent a red which becomes blue on washing; and chloriodide of zinc a violet blue. Millon's reagent readily dissolves collodion silk even in a cold solution.

1. J.S.C.I., 1909, 28, 1302.

2. Rev. gén. mat. color., 1909, 14, 14.

3. F.P. 408303, 1909.



**Chardonnet Silk** ("Besançon Silk," "Près de Vaux Silk," "Tubize Silk," "Nitro Silk," "Frankfurt Artificial Silk"). Although his first patent was taken out in 1884<sup>1</sup> little commercial progress was made until after the Paris Exhibition of 1889, where, notwithstanding the high inflammability of the product, the samples exhibited received a Grand Prix and excited much curiosity and admiration.<sup>2</sup> Chardonnet not only worked out methods of preparing acceptable cellulose nitrates for artificial filaments, but evolved and perfected the engineering detail connected with the mechanics of spinning and twisting the filament, and laid the foundation in a mechanical way for all those who have followed. He put into execution methods of transferring a liquid into a marketable thread in considerable quantities, and in this was distinctly a pioneer. The first experimental plant was located at Spreitenbach, Switzerland, but in 1893, due to interesting certain French capitalists, the experimental plant was removed to Besançon, France, where a long, tedious series of experiments on a commercial scale were carried on, which are reflected in the patents periodically issued, and which culminated in success. After the expenditure of vast sums of money in surmounting the obstacles—mostly mechanical—the plant became a noticeable commercial factor in 1899. From this time onward, progress was rapid and assured.<sup>3</sup> The original plant at Besançon started with an output of 50 k. a day in 1891; it had reached 1,500 k. in 1901, and 1,800 to 2,000 k. in 1907, and seems to remain at that figure in 1910.

1. F.P. 165349, 1884; the other Chardonnet patents are F.P. 172207, 1885; 199494, 201740, 1889; 203202, 207624, 208405, 1890; 216156, 216564, 1891; 221488, 225567, 1892; 231230, 1893; various renewals of the foregoing; E.P. 6045, 1885; 2210, 2211, 1886; 5270, 1888; 1656, 5376, 1890; 19560, 24638, 1891; 24638, 1893; D.R.P. 38368, 1885; 46125, 1888; 56331, 56655, 1890; 64031, 1891; 81599, 1893; U.S.P. 394559, 1888; 410104, 1889; 455245, 460629, 1891; 531158, 1894; Swiss P. 1958; 2123; 3667, 1891; 4412; 10506. It.P. 17844, 265, 1885; and First Addition thereto dated Jan. 5, 1887; Span.P. 7849, 1885; and Certificate of Addition thereto dated Jan. 20, 1886; Belg.P. 68890, 1885; Aust.-Hung.P. 31310, 1885. See also Chardonnet, C.R., 1887, 105, 898; 1889, 108, 962; see Pasqualis, It.P. 22846, 31932, 1892.

2. The first apparatus actually used by Chardonnet is shown in a photograph in "Fabrication de la soie artificielle parisienne," published by T. Foltzer in 1903. It is quite fitting that France, which has the silkworm industry so firmly established in the southern section, should foster and develop this artificial product. It has been stated that the instrumentality of L. Pasteur in saving the silkworm from threatened extinction by his bacteriological researches at a previous period, may have intensified the confidence of the French people in supporting this project through experimental vicissitudes to satisfactory commercial realization.

3. As an example of the peculiar difficulties encountered in attaining commercial success may be mentioned the failure of the English company, due, it was then said, to local atmospheric conditions, the actual solution prepared in France refusing to spin at the English (Coventry) factory. In the U. S., labor and tariff conditions were the two factors which deterred the French company from starting an American branch.

In the original Chardonnet process the liquid pyroxylin compound used to produce the weavable threads consisted of pyroxylin and a mixture of equal volumes of ether and alcohol.<sup>1</sup> The former was prepared by taking 100 gm. pyroxylin, 10–20 gm. of a metallic protochloride reducer (iron, chromium, manganese or tin) and 0.2 gm. of an oxidizable base such as quinine, aniline or rosaniline. For some mixtures 40% ether and 60% alcohol was found to yield the most satisfactory results. In order to prepare the liquid in the best condition, it was found preferable to dissolve the pyroxylin in the largest portion of the alcohol and ether, and in the rest of the solvent to dissolve the chloride, organic base and coloring matter (if any), the two solutions being subsequently mixed.<sup>2</sup> The nature of the pyroxylin

1. H. Wyss, *Leip. Farb. Ztg.*, 1898, (9), 47, 399; *Pap. Ztg.*, 1898, 23, 3824, 3863; *J.S.C.I.* 1887, 6, 139; 1888, 7, 206; 1889, 8, 539, 611; 1890, 9, 286; 1891, 10, 359; 1895, 14, 267; 1898, 17, 918. See Moyat, *Mon. Teint.*, 1892, 36, 50.

2. Where the pyroxylin was dehydrated by pressing rather than by the first method of drying until no further amount of moisture was removed, the pressed cake containing on the average 36% water, was introduced without further drying into horizontal slowly-revolving, tin-lined, cylindrical iron drums, and there treated with the solvent in the proportion of 100 l. combined ether-alcohol to 22 k. nitro-cellulose calculated on the dried product. The alcohol used being 95%, and estimating on a 36% moisture content in the pyroxylin, would give the spinning mixture an equivalent of about 7% water. This amount of water would increase the viscosity of the solution greatly, and was one factor contributing to the employment of high pressure to force the fluid through the orifices. The mixture of pyroxylin, alcohol and ether is slowly agitated for fifteen to twenty hours and then forced under a pressure of 30 to 60 atmospheres through a layer of carded cotton in specially constructed filter presses. This consists of a cylindrical vessel of about 100 l. capacity, the filtering material being placed on the bottom, and consisting of a layer of absorbent cotton 10 to 15 mm. diameter, and inclosed between two sheets of fine silk, which in turn are encompassed by two sheets of tinned wire gauze of 100–120 mesh. The pressure required is governed by the speed of filtration desired, the pressure being increased as the filter clogs in order that the volume filtered in a given time will be uniform, irrespective of the state of the filter. From these it passes direct into the storage tanks, which are of about 5,000 l. capacity, and in which it is allowed to "age" for what reason the author is not aware. It would appear to be more rational to allow the "ageing" process to take place before filtration, for upon standing the small insoluble particles tend to agglutinate together and a solution left to rest some time filters more readily, and clarifies more completely than a pyroxylin which has more recently been brought into solution. All the metallic parts of machinery, pipes, and tanks with which the pyroxylin solution comes in contact are tinned, and great care is taken throughout to avoid leakage of ether vapor. According to the *Soc. Anon. pour la Fab. de la Soie de Chardonnet* (F.P. 354398, 1905), the filters consist of cotton wool wrapped in muslin, and rapidly become impregnated with pyroxylin, owing to the evaporation of the solvent, and have to be renewed. Filtration is thus a burdensome operation, as the cotton wool and muslin are expensive, and the old caked filters have hitherto been burnt as a useless and possibly dangerous by-product. The process described is for the recovery of the cotton wool and muslin by treatment of these "filter cakes." Any solvent for pyroxylin or denitrating agent may be employed, but the best results are obtained by treatment at 70–90° with a 0.5% solution of sodium or potassium carbonate, or a 2–5% solution of an alkali sulphide. In this way the pyroxylin is dissolved, and may be removed with ease by a single washing with water. The cotton wool is left unaltered, and after being dried, and if necessary recombined, may be directly used again for filtering; or it may be nitrated. The dark-brown solution of the pyroxylin is evaporated, and the residue

used and the elasticity and strength one desires to realize in the threads produced from the fluid, will necessitate some variations from the general formula given above. The viscous liquid after filtration is drawn into threads by forcing through an orifice of about 0.5 mm. diameter in such a manner that the minute fluid stream, as it emerges from the spinneret, enters into a cold liquid such as water, which immediately coagulates and solidifies its exterior. The filament then presents the form of a tube or sheath, solid on its exterior and inclosing a central column of liquid which has not yet solidified. This filament, on account of its liquid interior, may be drawn or spun out into a fraction of its original size, provided the drawing operation is conducted before the interior of the filament congeals. After attenuation, it becomes solidified through its entire substance, this solidifica-

tion is calcined and converted into cellulose. The net cost of the process is stated to be insignificant, the plant rudimentary, and the labor practically *nil*. The operation may be carried out in any ordinary bleaching kier, and a particular form of the latter is described. From the storage tanks the pyroxylin solution is led in pipes still under pressure to the spinning room (see Fig. 120), where it is dis-

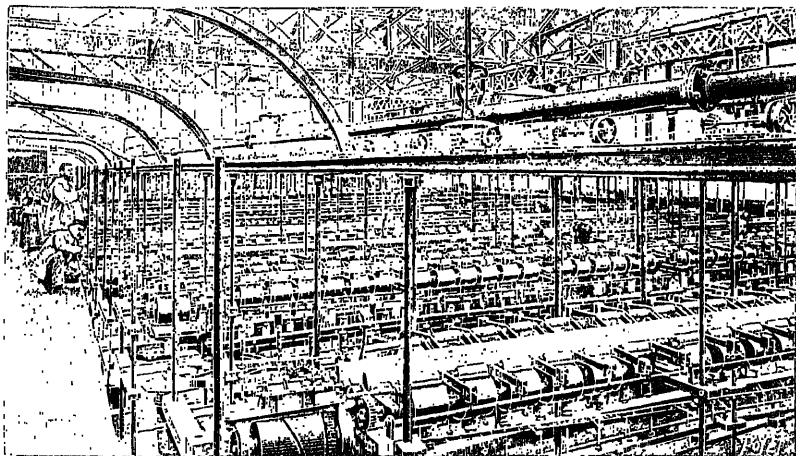


FIG. 120.—Conversion of Collodion into Artificial Silk (From Sci. Am. Suppl. No. 1156, p. 18470).

tributed in smaller tubes running along the spinning frames. These small tubes are provided with a number of reservoirs each of which ends in the small glass jets above mentioned. Where the nitrocellulose thread passes at once into a liquid coagulating media, as water, the process is spoken of as "wet spinning," whereas in the later processes, in which water is added directly to the spinning solution by means of incompletely dehydrated pyroxylin being used, the formed thread is coagulated in the air, this being known as "dry spinning." In order to form a thread, three or four of the original filaments are spun together, the further treatment of the product being analogous to that of natural silk, with the exception of the denitration process, applied before weaving.

tion being hastened by causing a circulation of warm air through an inclosed chamber in which the filaments are reeled. As the Chardonnet apparatus is the standard upon which subsequent modifications have been based, it is given in detail in the note below.<sup>1</sup> In

1. The apparatus is shown in Fig. 121, and in which appears a transverse section of the apparatus. Fig. 122 is a front elevation of a portion of the apparatus, the box or casing of the spinning apparatus being in vertical section. Fig. 123 is an enlarged fragmentary section of the working to Fig. 121, and showing the spinning devices. Fig. 124 is a fragmentary front elevation of the parts shown in Fig. 123;

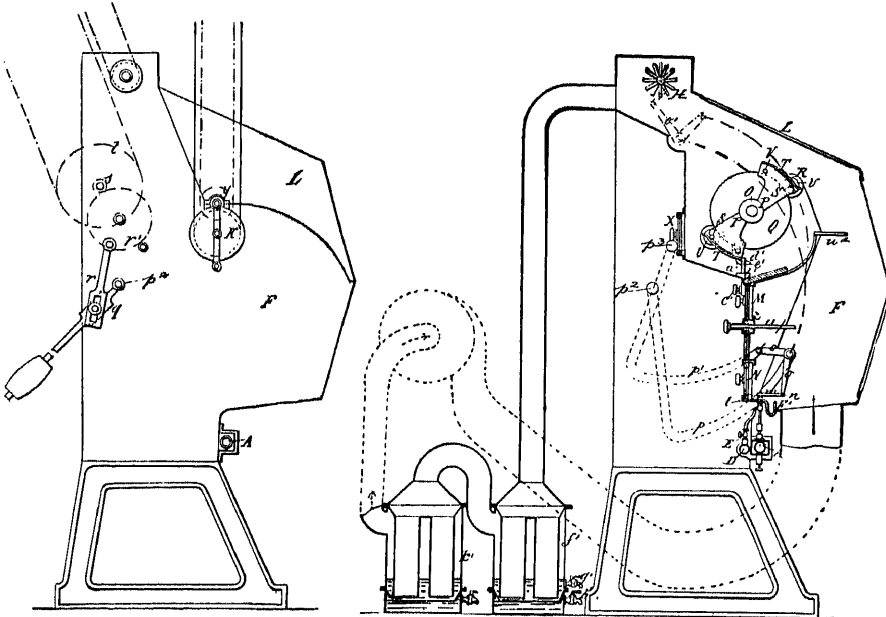


FIG. 121.—De Chardonnet Apparatus for Making Artificial Silk. (Transverse Section).

FIG. 122.—De Chardonnet Apparatus for Making Artificial Silk (Front Elevation).

a plan of the nippers *rr*, shown in Fig. 123 on the same enlarged scale, and a fragmentary plan view of the clamp *h* shown in Figs. 123 and 124. Fig. 125 is a side elevation of the apparatus.

The collodion solution, having been well filtered, is placed in a closed vessel or receptacle, *A'*. (Shown in Fig. 125.) This vessel is lined or coated interiorly with tin, and from it leads a pipe, *A*, which passes down toward the lower part of the machine and enters horizontally into the same, as shown in Fig. 122. This pipe is provided with a valve or stopcock, *B*, to regulate the flow. The closed vessel or reservoir is furnished with an air pump (not shown) which maintains in it a pressure of from two to three atmospheres, in order that the collodion liquid may be expelled with sufficient force to effect the spinning of the filaments. The pipe *A* extends through the entire length of the machine, wherein it is inclosed or partly surrounded by a water jacket, *C*, in the manner best shown in Figs. 121 and 123. In this water jacket, the walls of which are of thin metal, cold water is caused to circulate. The pipe *A* carries all the vertical spinners or nozzles through which the liquid is forced out to form the filaments. These spinners or nozzles *H* are arranged in a row equidistantly along the top of the pipe *A*. Each spinner

general, the method may be described as capillary spinning organs

is made up of several parts, as best shown in Fig. 123. On the top of the pipe *A* is a thickened boss, *b*, in which is formed a threaded hole, and into this is screwed a socket, *c*, in which is fixed a vertical tube, *d*, a thin packing, *e*, of rubber, vulcanized or not, being interposed around the tube *d* to make a tight joint.

To the upper end of the tube *d* is connected a flexible tube, *f*, of soft india-rubber or other impermeable material which cannot be attacked by the solution, and to the upper end of this flexible tube is connected a tube, *i*, of glass or other suitable material, the upper end of which is reduced to form a contracted nozzle or nipple. Around this nozzle is arranged a glass tube, *j*, which is held by a clamp, *k*, attached rigidly to a vertical slide *o*. This slide *o* extends downwardly and passes out beneath the inclosing case of the apparatus, and its lower portion, which is toothed,

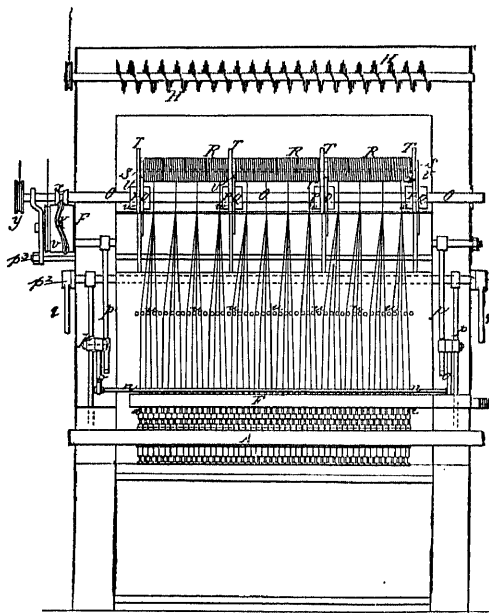


Fig. 123.—De Chardonnet Apparatus for Making Artificial Silk, Showing the Spinning Devices.

is engaged by a pinion, *p*, which is turned by a knob, *q*, at the front of the apparatus. By turning this knob the slide *o*, clamp *k*, and surrounding tube *j* are raised or lowered, while the nozzle tube *i* remains at the same height. Cold water enters by a tube, *l'*, Fig. 121, and is conducted by a flexible rubber tube, *l*, and the lateral branch *j'* into the interior of the tube *j* and around the nozzle tube *i*. The water that thus flows in ascends around the nozzle tube, runs over the top of the tube *j*, and runs down, being finally caught in a trough or gutter, *D*, Fig. 121. The flow of water is controlled by means of a screw clamp, *m*, which pinches more or less the rubber tube *l*, and thus reduces the size of the stream that passes through it. The clamp *m* is operated from the outside by means of a knob, *n*, at the front of the apparatus. In like manner the flow of the collodion liquid through the flexible tube *f* is regulated by the clamp *h*, which is adjusted by a screw, *g*, which extends out to the front of the machine, and is provided with a knob, *n'*. Fig. 124 illustrates this clamp in detail. Its construction is identical with the clamp *m*. Ordinarily the inclosing tube *j* extends higher than the nozzle tube *i*, as shown in Fig. 123, so that the collodion liquid on being forced out through the nozzle enters a body

surrounded by a water-filled tube, the working orifice of each spinning

of cold water held in the tube *j*, and is caused to pass through this water until it reaches the level of the top of the tube *j*; but when the machine is not in use it is desirable to close the nozzle, and it is also desirable that there shall be no water above it which might enter it. For this purpose the slide *o* is lowered by turning the knob *q*, thereby lowering the tube *j* until the level of the water therein is beneath the orifice of the nozzle. The same movement acts, by means of a link, *r*, to draw down an arm, *s*, pivoted at *s'*, the extremity of which carries a stopper or pad, *t*, which on being thus lowered closes said orifice in the nozzle and prevents the solidification of the solution in the capillary tube by the action of the surrounding air or by the water. The flow of water is shut off at the same time by turning the knob *n*.

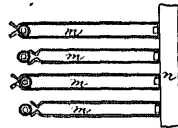
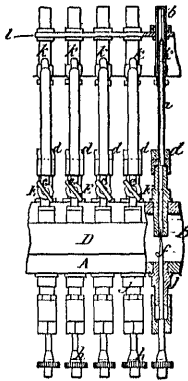


FIG. 124.—The de Chardonnet Apparatus for Making Artificial silk.

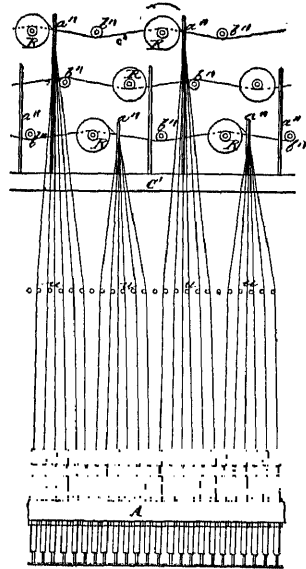
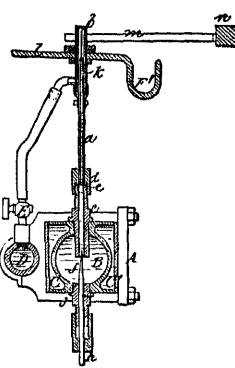


FIG. 125.—De Chardonnet Spinning Devices (Side Elevation).

In the operation of the machine the minute stream of collodion liquid on emerging from the nozzle is carried up through the tube *j* by the ascending stream of water, being solidified at the same time, and its end hangs or falls over the outside of the tube *j*. The loose end of the filament thus formed must then be grasped and carried to the reel in order that the spinning operation may commence. To accomplish this result the following mechanism is provided: The reel (shown at *K* in Figs. 121 and 122) is arranged in the upper part of the apparatus, with its winding-on side over the row of spinners or nozzles *H*. A long bar, *D'*, extends longitudinally in front of and a little above the row of nozzles and is fixed at each end to an elbow-lever, *E*. This bar *D'* carries a series of nippers or grasping fingers, *vv*, one to each nozzle. These nippers are best shown in Figs. 123 and 124. Each nipper is formed of two elastic springs curved as shown in side view in Fig. 123 and in plan in Fig. 124, and adapted to embrace the inclosing tube *j* of the nozzle. Both of the springs are fastened to the bar *D'* by one screw. The end portions of the springs are coated with soft india-rubber, not vulcanized. In Fig. 123 the nippers *v* are shown as engaging the tube *j*. If the bar *D'* were to be moved to the left in this figure, the springs would yield and the nippers would free themselves from

organ being surrounded by a pair of tweezers which transfer the fila-

the tube, at the same time engaging the overhanging end of the collodion filament. The bar  $D'$  is given such a movement that the nippers  $d$  travel first to the left and then, having freed themselves from the tube  $j$  and grasped the filament, sweep upwardly and over the top of the reel  $K$  in the path indicated by the dotted line  $xx$  in Fig. 121, thereby carrying the end of the filament up over the reel and enabling the reel to engage the filament and continue thereafter to draw it out. The speed of movement of the bar  $D'$  in its ascent and the speed of rotation of the reel  $K$  are so proportioned to the rate of discharge of the collodion from the nozzle that they act to draw out the filament to the proper degree of attenuation. In order to free the nippers from the filament after they have carried it over the reel, there is provided a revolving brush,  $J$ , the bristles of which encounter the nippers when the bar  $D'$  reaches its extreme upper position. By this means the nippers are cleaned. The bar  $D'$  is moved up and back two or three times per minute. At the completion of its downward movement its nippers  $vv$  spring over and embrace the glass tubes  $jj$ . During the upward movement of the bar its nippers carry the

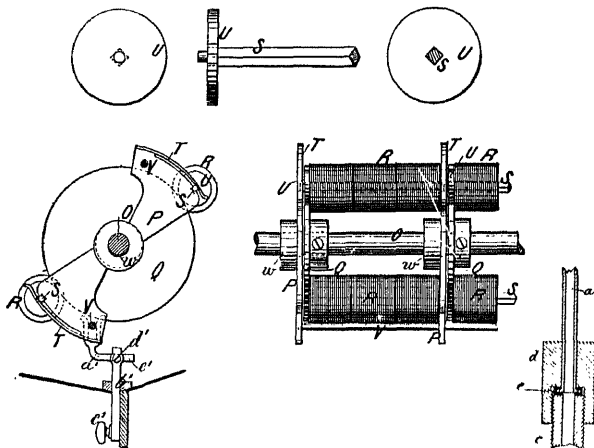


FIG. 126.—De Chardonnet Apparatus for Making Artificial Silk.

filament between horizontal guide pins,  $xx$ , which are arranged in a series corresponding to the number of nozzles, and the function of which is to separate the filaments emerging from the respective nozzles. Above the guide pins  $xx$  there is arranged a series of inclined guide pins,  $yy$ , as shown in Fig. 121, which are arranged in pairs, with the two pins of a pair converging, as shown in Fig. 122. The effect of this arrangement is that as the nippers carry the filaments up, the latter are first caught between the pins  $xx$  and thereby held distinct and parallel and the group of three filaments enters between the extremities of one pair of pins  $yy$ , and in being drawn down to the parallel portion, the three filaments are united to form one thread, which is then wound upon the reel.

The peculiar movement of the bar  $D'$  is imparted to it by a special combination of levers. At the commencement of the operation of the machine a filament will be forced out of reach of the nozzles  $II$ , of which there may be any number, and will flow over the top of the tube  $j$  of each nozzle. At the first movement of the bar  $D'$ , carrying the nippers, the filaments will be grasped by the nippers and elevated over the reel, and will then be engaged by the reel, after which they will be drawn or spun out without interruption. At the second movement of the bar  $D'$  the nippers will engage any filaments that may have been missed at the first movement, and will add them to the reel. Thereafter, although the movement of the bar  $D'$  continues, it is without effect so long as no interruption

ments to bobbins from which they are reeled off for the subsequent

occurs in the spinning of the filaments; but whenever a filament breaks the nippers *r*, which engage the nozzle corresponding to that filament, will grasp the overhanging end of the severed filament and carry it up over the reel again, whereupon the interrupted filament is reunited by adhesion with the others of its group. At each ascending movement of the bar *D'* the nippers are cleaned by the brush *J*.

In order that the successive turns of the thread on the reel shall not be wound upon themselves they cross angularly from side to side, thereby facilitating the drying of the threads. This is accomplished by imparting to the reel, in addition to its rotary movement, a longitudinal reciprocatory movement by means of the device shown in Fig. 122. A pulley, *L*, driven at suitable speed, carries a crank, which is connected to a pitman, *N*, which in turn is coupled to an oiler box, *O*. This box is mounted on the shaft *P* of the reel, being confined thereon between collars *zz*, so that the shaft is free to turn within the box; but as the box is moved endwise the shaft is carried with it. The shaft *P* may be rotated by a belt passing over a pulley, *P'*, or by any other means. The pulley *P'* is connected with the

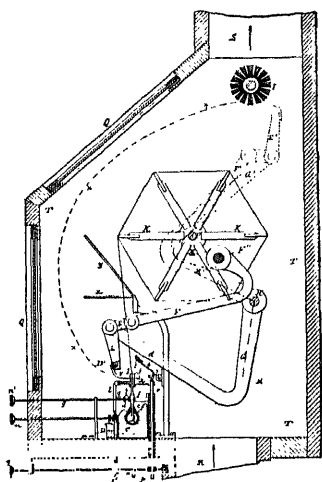


FIG. 127.—Improved Chardonnet Process for Artificial Silk Manufacture.

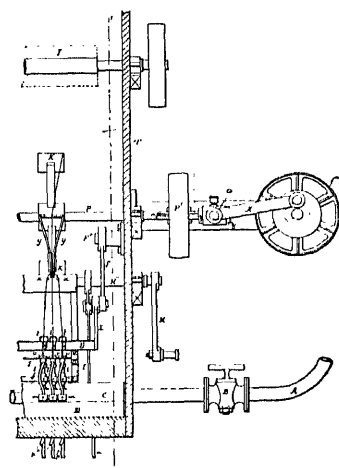


FIG. 128.—Improved Chardonnet Process for Artificial Silk Manufacture.

shaft by a key and groove, so that the shaft can slide freely and still be rotated by the pulley. The pulley is prevented from sliding with the shaft by means of fingers which embrace its rim, the fingers being supported by the bracket which supports the pulley *L*. (See Figs. 122 and 125.)

The entire apparatus, with the exception of the regulating knobs, is inclosed in a suitable tight box or casing, *T*, provided with glazed openings *QQ*, through which the operator may look in order to observe the operation of the machine. These may be opened in order to regulate or clean the apparatus. A current of air is caused to circulate through the box, *T*, entering at *R* and passing out at *S*. For this purpose a fan or blower, *S'*, Fig. 125, may be provided. This air, which should be heated to about 30° C., serves to dry the threads and carries away with it the spirituous and aqueous vapors which are evaporated within the casing. These vapors are subsequently recovered by passing the air through water or through a refrigerating machine. The air is then reheated and reintroduced at *R*. It thus circulates continuously. The alcohol and ether are separated from the water by rectification, or by fractional distillation, and serve, without being separated from each other, for dissolving the pyroxylin for forming the collodion solution.



treatments. The object of the introduction of metallic chlorides

The improved Chardonnet process is shown in Figs. 127 to 130 inclusive, in which the collodion solution, well filtered, is introduced into a closed vessel (not shown in the drawings) in which an air pump maintains a pressure of from six to twelve atmospheres. This vessel, suitably lined inside, communicates through a stop-cock with the pipe *A*, which carries the spinning dies, and extends the whole length of the machine, being arranged underneath the casing *P*, which incloses the spinning and reeling mechanism. The pipe *A*, as shown in detail to an enlarged scale by Fig. 129, has three internal compartments, the central one *B*, which holds the solution and forms a conduit for conducting it to the spinning dies, and the two side compartments, *C* and *C'*, for circulating water around the central tube *B*. Each spinning die consists of a tube *a*, on which is soldered a capillary tube *b*. The lower end of tube *a* communicates with the sleeve *c* screwed into the pipe *A*, the mouth of which sleeve opens into the conduit *B*. A screw union *d* holds the die tube to the sleeve, making a tight joint by two washers of leather or the like, pressing between them the lip *e* at the lower end of the tube *a*, as best shown in Fig. 130, and constituting thus a detachable coupling for uniting the die *a* to the

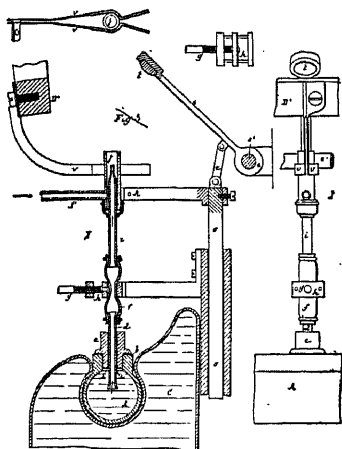


FIG. 129.—Improved Chardonnet Process for Artificial Silk Manufacture.

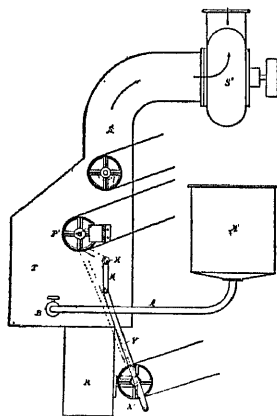


FIG. 130.—Improved Chardonnet Process for Artificial Silk Manufacture.

supply tube or sleeve *c*. The outflow of the liquid from the conduit *B* into each of the die tubes is regulated by the conical end *f* of a screw pin or rod *h*, which enters the lower end of the sleeve *c*, and by means of an adjusting head beneath the pipe *A*, so as to diminish or increase the area of the passage through which the liquid flows into the die tube. The valves thus constructed enable the flow to the separate dies to be regulated with great nicety, and in connection with the detachable couplings provide for the shutting off of the flow from any die that may become clogged, and its removal and replacement without interfering with the spinning from the remaining dies. These valves are made of metal or other material not acted on by liquid, and their adjusting heads project beneath the casing *P*, where they are readily accessible and within easy reach of the operator. Around the upper part of each die tube is a casing *k*, supported by the fixed plate *l*, which extends along the machine. The casing *k* supplies cold water at the end of the die tube, this water being supplied from a pipe *D*, which has a branch with stop-cock *E* to each of the casings *k*. These stop-cocks, which are made of metal, regulate the flow of cold water in which the filament is submerged as it issues from the die tube *a*, instead of regulating this flow by the compression of a rubber tube, as formerly. The overflow water runs into a gutter *F*.

and alkaloids was to reduce the inflammability,<sup>1</sup> but this having been found ineffective, later gave way to denitration of the nitro-cellulose.<sup>2</sup> In a subsequent process, the diameter of the spinnerets (glass tubes called "silk worms") is reduced to about 0.08 mm., this necessitating increase of pressure to 50-60 atmospheres in order to force the solution (containing from 10-20% cellulose nitrate) through the spinning orifices at the desired rate of flow. Whereas at first a pyroxylin dried until no further loss of weight occurs was taken to prepare the fluid used in spinning, it was subsequently found that this solution was so high in solvent as to be difficult to dry without contortion of the fiber. The pyroxylin, therefore, instead of being dried—which was a source of considerable danger—was dehydrated by pressure and used while still containing from 30-40% of water. As the result of the additional water left in the pyroxylin, it was found that exposure of the formed filaments to air at a temperature of about 50° was sufficient to eliminate the solvent from the filament, and this obviated the necessity of washing in water, which often caused the thread to become opaque and decrease in tensile strength.<sup>3</sup>

1. U.S.P. 410404, 1889; F.P. 188304, 1888; E.P. 5270, 1888. The spinning apparatus was originally so arranged that the emerging threads were plunged into water containing 0.5% nitric acid, but this acid wash was soon found to be superfluous. Usually 500 m. is the length wound on each reel, the thread being then taken off and brought together to a skein. Definite knowledge is lacking as to the amount of solvent evaporated per unit weight of silk obtained in this process. E. A. Mangin, representing the Chardonnet Artificial Silk Co. in America, at the hearings before the Committee on Ways and Means of the U. S. House of Representatives, 59th Congress, First Session, Feb.-Mar., 1906, p. 68, testified that the French company used ethyl alcohol denatured with ether, having found it impossible to employ wood alcohol; paid 40-45 cents per gallon for the alcohol; could produce Chardonnet silk in the United States with denatured alcohol for \$1.25-1.50 per pound; that 1-1.5 gal. alcohol are used per lb. of finished "silk" manufactured. This amount appears excessive if the pyroxylin produced is of low viscosity, as undoubtedly the nitrating process would be adjusted to produce a very fluid pyroxylin from the economical point of reducing to the minimum the amount of solvent required.

2. Chardonnet's method of denitration (U.S.P. 410404, 1889; F.P. 188304, 1888) is to maintain the pyroxylin at 30°-35° in a bath of nitric acid of density of about 1.32, the complete transformation being recognized either by analysis, solubility test or by observing the commencement of softening of the pyroxylin fibers. See U. S. Consul's Report No. 150, Mar., 1893, p. 402; *abst. J.S.C.I.*, 1893, 12, 516.

3. After spinning, the filament still contains a small amount of alcohol and water, being entirely dried by hanging in the form of hanks in a closed chamber and exposing to a powerful current of air heated to 45°-50°. Of the finer qualities of the fiber, 220,000 m. weigh but 1 k. Hörk and Druge obtain more uniform results by the use of a less aqueous pyroxylin than described by Chardonnet. Turgard (F.P. 344845, 1904) dissolves 100 gm. pyroxylin in a mixture of 2,400 cc. alcohol 90-95% strength and 600 cc. glacial acetic acid. After the pyroxylin has been dissolved there is added 5 gm. castor oil and 3 gm. albumin, when the mixture is ready to be formed into filaments.

According to C.R., 1889, 108, 961, the sulphited pulp of young wood is used as the source of cellulose, being first disintegrated in a carding machine in order to form a light and very bulky fleece, similar in appearance to cotton waste. After

The artificial silk manufactured by the Chardonnet factories after proper bleaching and drying under tension is at least as white as natural silk, and has been claimed as even whiter, when both are compared in a Lovibond tintometer, or an F. Ives colorimeter. It possesses in a smaller degree the characteristic crackling rustle of natural mulberry silk, but feels somewhat firmer than this. According to the statements of the inventor, its density is equal to 1.49, while that of Grege silk is 1.66, and of boiled mulberry silk 1.43. According to Herzog<sup>1</sup> the sp.gr. is about 13% greater than natural silk. Chardonnet gives its strength of flexure as 25-35 k. per sq. mm., about 20% less than boiled silk. The elasticity is about that of natural silk, the extension of the threads amounts to 15-20% and the real elasticity to 4-5%. Herzog makes the following comparison of the

drying at 140-160°, the hot mass is immersed in the nitrating acid in earthenware vessels. Comparative experiments have shown that nitrocellulose prepared from wood pulp, while it gives a more fluid solution when dissolved in alcohol and ether, the product obtained after spinning has an inferior tensile strength and is stated to lack the luster and purity of color of the filaments produced from cotton as the source of cellulose. It is claimed (E. Opfermann, E. Friedemann and Act.-Ges. für Maschinenpapierfabrikation, F.P. 402462, 1909; E.P. 10604, 1909; D.R.P. 219085, 1909; abst. J.S.C.I., 1909, 28, 1270) that the impurities in wood pulp which limit its application in the manufacture of artificial filaments and nitrocellulose may be extracted by boiling the cellulose pulp under pressure with a solution of sodium carbonate at a concentration of 0.5-2%, with the addition, if the case seems to demand it, of small proportions of alkali hydroxide or sulphide. Or else the pulp may be boiled with a solution containing 10 gm. of calcium oxide per l. By this treatment incrustations, wood gums, and resin are dissolved and at the same time, in the subsequent bleaching, a saving of about 50% of the bleaching agent is realized. According to the property of the fiber employed the concentration of the alkali lye is about  $\frac{1}{2}$ -2%, heating for about three to six hours at a pressure of about 2-3 atmospheres. A small addition of caustic alkali or alkali sulphide increases the softness of the product without weakening it.

The manufacture of the glass spinneret tubes, the orifice of which is invisible to the naked eye, is one of the most delicate parts of the work. The uniformity of the threads issuing from them is dependent upon the exactness with which the apertures approximate the same diameter. Glass tubes are heated to redness and quickly pulled out, it being impossible to pull a glass tube out so fine that it will not have a hollow interior. The glass is cut off as near to the required diameter as possible with the unaided eye and experience, but are afterwards standardized by measurements under the microscope with a micrometer, and only those tubes accepted which vary within an established limit from the diameter sought, those of wider or narrower apertures being rejected, although the narrow aperture tubes may be made to the desired larger internal diameter by carefully removing the end by grinding on a fine stone. In those processes in which the spinnerets are microscopic holes in platinum sheets, they are said to be cut by very fine dies. It is evident that it must be exceedingly difficult to produce with exactness an invisible orifice.

The statement is made that in 1907 2,500,000 l. of alcohol were consumed in the Besançon works, so that each k. required between 4-5 l. of alcohol in its manufacture. A k. of 100 denier thread of this silk contains 90,000 m. in length, or nearly 2,000,000 m. of single filament as squirted from the jets. The selling price of this product has been given as 30 fr. per k. in 1896, 26.50 fr. in 1897, and 21.75 fr. in 1898; in 1903 it reached the price of 40 fr. per k., and it may be taken at 20 fr. in 1910.

1. Lehne's Farb. Ztg. 1894-5, p. 49.

firmness of Chardonnet silk: 60 denier titer, 69 gm. strength; extension, 155 mm. to 1 m.; 65 denier titer, 83 gm. strength; extension 171 mm. to 1 m. A boiled Minchew wool—one of the cheapest natural silks—gave 214 gm. strength and 189 mm. to 1 m. extension. According to Silbermann<sup>1</sup> the following figures represent equal titer: Real silk 38, Tussah 48, Chardonnet 17. Chardonnet gives the thickness of a single thread as 12–20  $\mu$ . Blanc states the thickness varies from 20–45  $\mu$ , and Silbermann has noticed threads of 52–60  $\mu$  in diameter. This variation in observations is explicable in the varying thickness of the individual filaments, due to the tension exerted after forcing the fluid out of the spinnerets and before coagulation has taken place. In Chardonnet silk the single filaments are united to a thread of desired size by torsion only, and without the aid of a cementing agent. Nitrocellulose silks, like cellulose nitrate, become electrical when rubbed.

**F. Lehner's Artificial Silk**<sup>2</sup> differs in many essential particulars from that produced by the previously described Chardonnet process. Whereas Chardonnet used viscous solutions and pressures as high as 60 k. per cm. and with concentrations as high as 20% pyroxylin, Lehner works with 10% solutions and reduces the pressure materially by means of the addition of small amounts of mineral acids as sulphuric, whereby the viscosity of the solution is greatly diminished,<sup>3</sup> this being attributed to molecular change.<sup>4</sup> In one modification of the Lehner process, there is taken silk waste of all kinds, including the flake waste products formed in the process of spinning floss silk. These remnants and wastes are thoroughly cleansed and digested for twenty-four hours with a concentrated solution of caustic potash or soda, or cuprammonium oxide, the silk substance being dissolved. The solution thus obtained is filtered, diluted with water, neutralized with an acid which slowly precipitates out the silk substance (a mixture of fibroin and sericin) in the form of fine threads of a pale reddish color. The precipitate thus obtained is well washed with cold water, the latter removed and the solid dissolved in concentrated acetic acid in the proportion of 1 to 5, this constituting

1. "Die Siede," 1897, **2**, 143.

2. For statement on Lehner Silk see U. S. Consular Report, Dec., 1894, 538; abst. J.S.C.I., 1895, **14**, 83, 405. Chem. Zeit., 1906, **30**, 579; Zeit. ang. Chem., 1906, **19**, 1581; Wollen. Z., 1892, **24**, 707; C. Bl. Text. Ind., 1894, **25**, 393; Mon. Text. Ind., 1892, **7**, 101. Although Lehner demonstrated his process in London, it was in Switzerland that he built up the business associated with his name.

3. U.S.P. 559392, 1896; D.R.P. 55949, 1889; 58508, 1890; E.P. 11831, 1891; It.P. 27943, 1890; Aust.-Hung.P. 54062 and 9475, 1891; Swiss P. 3710, 1891. See Koechlin, Soc. Ind. de Mulhouse Sitzungs, 1889, pp. viii+22; abst. J.S.C.I., 1889, **8**, 611.

4. Chardonnet, F.P. 231230, 1893.

"solution A." The second solution or *B*, is obtained by macerating for fifteen minutes cellulose, silk-paper, cotton or spinning wastes in an ammoniacal copper solution, the solution being expressed, and the washed residue nitrated in the usual way. The nitrocellulose so obtained is now dissolved in a mixture of methyl alcohol or ether and ethyl sulphuric acid, preferably in the proportion of 3 parts of the former to 1 of the latter.<sup>1</sup> The nitrocellulose is dissolved in this mixture of wood alcohol or ether and ethyl sulphuric acid in the proportion of 8 parts of the former to 100 of the latter, and maintained at 30° for one hour. A denitration of the dissolved nitrocellulose takes place under these conditions, nitroethane being evolved and escaping. Solutions *A* and *B* are then united in such a way that 5 parts of nitrocellulose are combined with 1 of silk fibroin, from which mixture the artificial silk filament is formed by allowing the

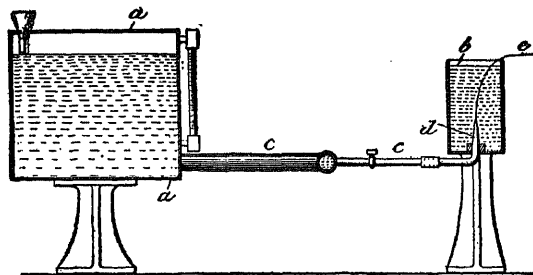


FIG. 131.—The Lehner Process of Making Artificial Silk.

mixture to pass through a small opening into a coagulating medium, preferably oil of turpentine, benzine, benzene, and other liquids free from oxygen.

The apparatus for carrying out this process is shown in Fig. 131, in which *a* represents the tank for containing the mixture of the solutions *A* and *B*. *b* represents the vessel containing the coagulating or solidifying liquid. A pipe *c*, provided with a suitable cock or other regulating device, communicates with the tank *a*, and is provided with an outlet or small orifice *d* at or near the bottom of the vessel *b*, through which the liquid mixture from *a* passes into the liquid contained in the vessel *b*, below the level of the said liquid. This orifice *d* is located below the level of the liquid in the tank *a*, so that it will be forced into the coagulating liquid under a certain head or pressure. The liquid from *a*, as it passes through the liquid in the vessel *b*, is coagulated or solidified and formed into a thread *e*, which is drawn

1. The ethyl sulphuric acid used in the process was obtained by mixing 2 parts strong alcohol with 1 part sulphuric acid, 60° Bé., and gradually heating to 100°.

forth from the congealing-bath and spun and wound by suitable machinery.

Lehner has attempted to insure uniformity in his product<sup>1</sup> by isolating certain of the cellulose nitrates (tri- and tetra-) and eliminating the other lower and higher nitrates.<sup>2</sup> Sulphuric acid is added to increase the fluidity, a vulcanized vegetable oil is incorporated in the mixture, the whole dissolved in acetone or ether-alcohol, and after spinning, immersing the thread for a long time in running water, after which the filament is denitrated with an alkaline sulphide containing a neutral magnesium salt. The denitration is conducted at a temperature of 40° and continued until "the rainbow colors of cellulose are visible under the microscope in polarized light."

In a later process<sup>3</sup> resins such as copal, dammar and sandarac are made use of in combination with an oil as linseed, together with nitrocellulose, and an inorganic salt to render the fiber incombustible. The filament is formed by combining the following three solutions in the manner stated:

Solution 1 is formed by dissolving 500 gm. finely pulverized resin (copal, sandarac, or the like) in 2,400 gm. of ether, shaking the mixture thoroughly at a moderate temperature in a well-stoppered bottle, and permitting the same to stand several days until it becomes clear. The clear solution is then poured off or decanted and mixed with 100 gm. linseed oil and then filtered.

Solution 2, the cellulose solution, is prepared by immersing silk-paper, cellulose, cotton, or wastes from spinning for about fifteen

1. U.S.P. 562626, 1896. In order to produce a perfectly homogeneous mixture of nitrocellulose Lehner found it "necessary to gradually add the cellulose to the nitrating bath," the temperature of the bath being raised cautiously as the nitration proceeds. After the completion of nitration, the product is centrifuged from a portion of the nitrating acids, not washed with water, but immediately plunged into sulphuric acid and again subjected to centrifugal action, the acid-wet resultant mass being then mixed with a vulcanized oil "for the purpose of maintaining the otherwise unstable nitro compounds unchanged." The vulcanized oil was prepared by taking a drying oil as cotton seed, poppy, linseed, or nut oils, treating with half its weight of sulphuric ether in order to modify the reaction, after which is added sulphur chloride in amounts from 10 to 20%, depending on the nature of the oil employed, the mixture being continually agitated during the slow introduction of the chloride. After a short time a yellow precipitate settles out, leaving a clear liquid which is decanted and mixed with nine times its weight of the wet nitrocellulose, the whole mixture being then dissolved in about 5 times its volume of alcohol and ether. After filtration, this constitutes the raw material from which the threads are spun. In vulcanizing vegetable oils with sulphur chloride, care must be taken to keep the temperature down to 20°, or better lower, and to use the minimum amount of chloride, or the resulting product formed will be insoluble in alcohol, ether or acetone, alone or combined.

2. U.S.P. 562732, 1896; 724020, 1903; D.R.P. 82555, 1894; F.P. 221901, 224460, 1892; 243612, 243677, 1894; E.P. 22736, 1892; 24003, 1893; 24009, 1894; 2595, 10868, 1896; Sw.P. 4984, 1892.

3. E.P. 20461, 1900.

minutes in a solution of cuprammonium oxide obtained by dissolving 10 parts sulphate of copper (blue vitriol) in 100 parts of an aqueous solution of ammonia having the sp.gr. 0.975. The cellulose substance is added to the cuprammonium oxide solution in the proportion of about 1 k. of the former to 12 l. of the solution. In some instances a 5% alkaline solution, such as a solution of caustic potash or caustic soda, may be employed in lieu of the cuprammonium oxide solution. The function of the cuprammonium oxide solution is to facilitate the subsequent nitration. The mass is then removed from the bath, thoroughly washed in much warm water, expressed, and finally well dried. It is then transferred, in as flaky a condition as possible, into a mixture of 4 parts sulphuric acid having a sp.gr. of 1.84, and 3 parts of nitric acid of sp.gr. 1.4, the mixture being heated to 75°. It is well stirred in the bath and the acid is poured off after five minutes. The nitrocellulose so obtained is thoroughly washed with water, dried, and wood spirits is poured over in the proportion of 9 parts by weight of the former to 1 part of the nitrocellulose. This mixture is thoroughly shaken until all the nitrocellulose has passed into solution. The solution is then set aside in a cool place for about eight days, until it has become clear, when it is poured off or decanted from the sediment.

Solution 3 is prepared by dissolving 100 gm. of sodium acetate (or of ammonium salts) in 1,000 gm. of dilute alcohol. This solution of an alkali salt is for the purpose of rendering the resultant fiber or thread incombustible.

The above three solutions are now mixed so that 1 k. nitrocellulose is combined with 200 gm. resin, 50 gm. linseed oil, and from 100–200 gm. sodium acetate (or salt of ammonium). The mixture so prepared forms the ground solution or liquid from which the threads or fiber constituting the artificial silk are formed. This may be done by simply causing the liquid to flow into the atmosphere upon a rotating cylinder or upon a moving smooth surface, whereby the solvents are evaporated, leaving a filament of the artificial fiber upon the surface consisting of nitrocellulose combined with a resinous substance and oil. In order to produce a thread or fiber having the characteristic luster and the other prized qualities of silk, the ground liquid should not be allowed to pass directly into the air but through a fine tube into a bath of some solvent of the solvents employed in the three component solutions, consisting of liquids which contain neither water nor oxygen, which would have an oxidizing reaction. Such a bath may consist of oil of turpentine, oil of juniper, benzine, benzol, petroleum, or generally of a liquid hydrocarbon. Were the thread,

as it issues from the orifice under the bath, drawn through a solution or congealing-bath of water or containing water or oxygen, it would not possess the luster and other desirable qualities of the silk. When, however, the liquid is made to pass under a congealing-bath of one of the above liquids (which is done by causing the liquid to issue through fine orifices having a bore of  $\frac{1}{2}$  mm., and under a slight pressure caused by having the level of the bath elevated a few centimeters above the orifices) a thick filament is formed, which may be drawn fine within the bath, and be reeled and spun.

The mechanical portion of the process is shown in Figs. 132 and 133, in which letter *A* represents a tank having a gauge *a*, and adapted to be filled with the mixture described, that should be kept at approximately the same level. The mixture flows out of tube *B* and trans-

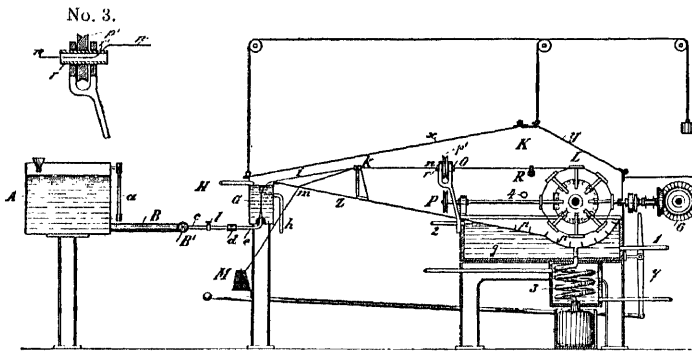


FIG. 132.—The Lehner Apparatus of Making Artificial Silk.

verse tube *B'* into a number of smaller tubes *c*, each of which carries a cock *l*. To these tubes there are connected, by rubber couplings, *d* the bent glass tubes *e*, drawn out somewhat to a point and entering from below a narrow tank *G*. The glass tubes pass through a proper packing into the tank, to prevent leakage. The tank *G* is filled with the congealing-bath described, such as oil of turpentine, petroleum, and should have a somewhat lower level than tank *A*. By this slight difference in pressure a mixture is ejected from tubes *e*, either in the form of thick threads or in the form of gradually increasing lumps that form upon the ends of the tubes. The lump is caught by a wire and drawn slowly out of the tank *G*, over guide *k*, through twister *O* and guide *R* upon reel *L*. This reel thus steadily draws the thread *i* out of tank *G*, the fineness of the thread being proportional to the velocity of the reel. The thread on leaving the tank is thick and soft, but rapidly grows thin within the tank. Fresh liquid is continuously



added through inlet *H*, while the liquid mixed with the solvent flows off through exit *h*.

The threads *i* may be united with one another or with a thread *m* of a different material at the tubes or guides *k*. The thread *m* passes from reel *M* and is simultaneously reeled with thread *i* upon

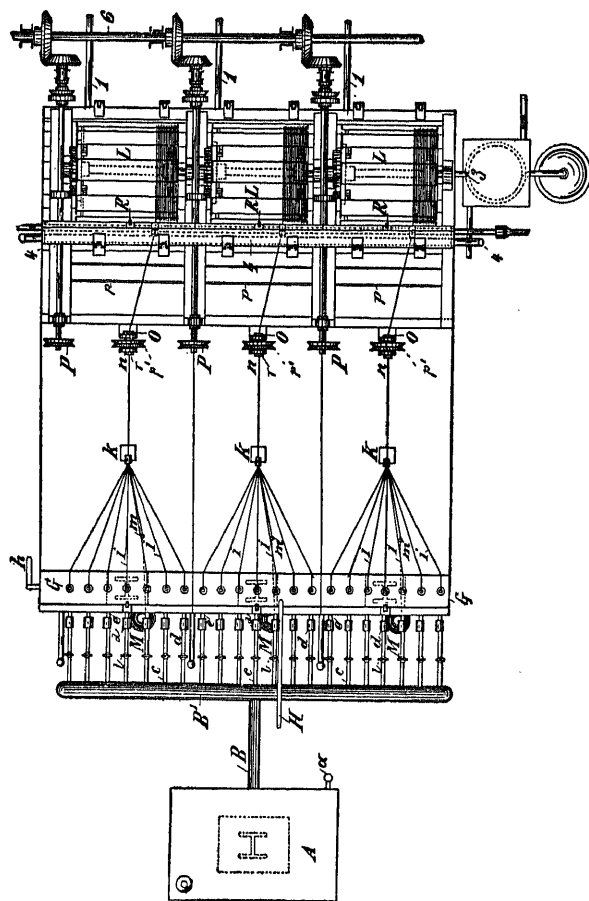


FIG. 133.—The Lehner Apparatus for Making Artificial Silk.

reel *L*. The bottom *Z* of the apparatus has a small perforation through which the thread *m* is admitted. When a spool *M* is run down, it is at once replaced by a full spool.

The threads united at *k* enter the twister *O*. This twister consists, essentially, of a rapidly rotating tube *r* (see particularly Fig. 132, No. 3), having a lateral opening *r'*, i.e., an opening in its periphery.

The thread enters the bore of the tube and leaves the same through the lateral opening, so that the revolution of the tube causes a twisting of the thread. This twisting of the thread is permitted for the reason that the end of the thread at the orifice of the tube *e* is still in a liquid or semi-liquid condition and is, hence, not held fast at this point. Upon the tubes are mounted the pulleys *p*, that are driven by a belt (not shown) from the pulleys *P*. These pulleys receive their motion from a power-shaft 6 by suitable gearing. The reels *L* continually draw the thread through the twister out of the tank *G* and off the reel *M*. Between the reel *L* and twister *O* a thread-guide *R* is arranged which has a reciprocating motion and places the twisted thread upon the reel in the proper manner.

The threads *i m* are united in a closed chamber *K*, which also contains the twister *O*, thread-guide *R*, and reel *L*. To this chamber ready access may be gained by means of two hinged windows *x* and *y*. The floor *Z* of the chamber serves as a condenser for the solvent still adhering to the threads. The floor is provided with partitions *p*, Fig. 131, which accelerate the condensation by presenting a greater cooling-surface. A large portion of the floor is in contact with a basin *q*, filled with cold water, which continually enters at 1 and, when warmed, leaves at 2.

The condensed solvent passes from the floor through cooling-coil 3 and is collected at the end. To rid the threads as much as possible from these adhering matters, a heating-tube 4 is passed through the apparatus. Through this tube there flows a stream of hot water, so that the upper part of the apparatus is heated.

Lehner's success appears to be due to the fact that he circumvented, rather than overcame the obstacles which confronted Chardonnet and his colleagues, his processes being distinguished for their comparative simplicity, both from a mechanical as well as a chemical point of view. On account of working with lesser pressures than Chardonnet, Lehner was enabled to produce finer threads from a given aperture because the total pyroxylin in the solution was reduced about half as compared with the Chardonnet methods, and this upon evaporation produced finer threads, of consequently greater luster. In Switzerland, Lehner established and built up the large works associated with his name, and which daily turn out of the nitro-silk amounts estimated at about 2,800 lb. By using water as the coagulating medium, Lehner was able to recover a large portion of the solvents used. Lehner silk exhibits a close similarity to the Chardonnet filament, being more regular in outline in cross-section, a round, pseudo-tubular form prevailing as the result of the conditions of shrinkage and collapse

of the fiber in elimination of the solvents with the subsequent dehydrating. The constants for "breaking strain" both in the moistened and air-dried condition, in elasticity, resiliency, etc., closely approximates the filament of Chardonnet.

Artificial silk manufactured according to the Lehner process is of an even white color, very beautiful gloss, and soft silk-like feeling. When crushed together it also shows somewhat of the crackle of real silk. According to Silbermann it is only about 7-8% heavier than real silk, its firmness being in proportion to that of Italian mulberry silk as 68:100. According to measurements of Thiele, a weakly twisted thread of Lehner silk of 0.5 mm. length, which contained 200 single fibers, broke at an extension of 44 mm. and 1,400 gm. strain. A weakly twisted thread of organzine of  $\frac{1}{2}$  mm. length, which contained 840 singles fibers, broke at an extension of 65 mm. and 1,340 gm. strain. Accordingly the greatest strain for the single fiber was—for Lehner silk 7 gm., for organzine 1.6 gm. The diameter of the artificial silk was about 2.5 times as great as the tested natural silk. The fiber should have a 6-fold cross-section and the highest strain for fibers of equal cross-section should give the following figures: for Lehner silk 7 gm., for organzine 9.6 gm. The frangibility for Lehner silk should be about 30% less than that of organzine. Like Chardonnet silk, Lehner artificial silk loses firmness by moistening, yet dyeing causes no difficulties.

According to claims of the inventor and the corroborations of literature the combustibility of Lehner silk is no greater than that of cotton.<sup>1</sup>

1. The following is an official report on the properties of Lehner silk:

Bradford Corporation Conditioning House, June, 8, 1894.

a. The samples submitted to me are purely artificial, containing no filaments of pure silk.

b. The relative strength, compared with Italian pure silk of the same counts (4,010 yards to the ounce), is as 68 to 100.

c. Pure silk has but little elasticity, and when stretched does not go back to its original length; neither does the artificial silk, but its stretching quality (before breaking) is as 73 to 100 relatively.

d. Taken at a denier, measure for measure, the relative weight of the same average diameters of pure and artificial silk is 7.25% more in the latter, which corroborates the relative specific gravities of each.

e. The artificial silk is much even in counts (taking 20 tests of 10 yards each) than any pure silk.

f. The denitrated artificial silk takes the dye in all shades perfectly even and brilliant.

g. It stands boiling, washing off, and the use of either acids or alkalies equally well as pure silk.

h. The gloss or luster is equal to the best silk. Its appearance, and therefore decorative value, is far above spun chappe or combed silks.

i. In its denitrated state it is less inflammable than cotton, and perfectly safe for storing in quantity, either raw or dyed, and it is less inflammable than any sample of denitrated "artificial silks" we have yet tested.

WALTER TOWNEND, Manager.

**J. Du Vivier Silk, also Termed "Fismés Silk,"** was first produced in 1889 in France.<sup>1</sup> It has been described as essentially the same as that of Chardonnet, but a closer inspection of the process will show that there are many new ideas embodied in the methods of Du Vivier. The nitration of the cotton is carried on with dry potassium nitrate (saltpeter) and sulphuric acid, instead of the customary mixture of nitric and sulphuric acids, and at the comparatively high temperatures of 60–80°. The slight solubility of the potassium sulphate formed in the reaction necessitates a larger amount of water in neutralization than with nitric acid as the nitrating acid, but otherwise the finished product is the same. The nitrocellulose is combined with gelatin or albumen, this being the distinct difference from the Chardonnet method, by which, chemically, the product more nearly approaches that of natural silk, the gloss and luster is increased, but the tendering when wetted is also increased, due to the presence of the gelatin. A solvent of both gelatin and nitrocellulose is required, glacial acetic acid being used. The preferred composition consists of nitrocellulose 96, gelatin or isinglass 2, albumen 2, total 100, dissolved in glacial acetic acid 1,600 (all parts by weight). Hence approximately a 6% solution of total solids is considered by Du Vivier as the best concentration for spinning purposes.<sup>2</sup> After the threads have been formed by expression through orifices under water, they are carried through a coagulating bath of sodium bisulphite and afterwards denitrated in hanks. In the various patents taken out by Du Vivier are unessential modifications and additions of the above process, but it is understood that they were not worked on a commercial scale. The addition of gutta percha in carbon bisulphide, passage of the filaments through a mercuric chloride bath and then through an atmosphere of carbon dioxide are some of the procedures suggested. The presence of the albumen and isinglass so tendered the filament, especially in the dampened condition, that, although the appearance and luster were entirely satisfactory, the product does not seem to have passed much beyond the experimental stage, and so far as the author is aware, is not at present manufactured on a commercial scale.

1. F.P. 195654, 195655, 195656, 1889; 208856, 208857, 1890; E.P. 2570, 2571, 1889; U.S.P. 563214, 1896; Belg.P. 84774, 1889; Span.P. 9204, 1889; It.P. 356, 1889; D.R.P. 52977, 1890.

2. As albumen is insoluble in acetic acid, to its aqueous solution is added "slightly carbonated soda" in amount about 35% of the weight of albumen. The mixture obtained is mixed, desiccated at below 20° in order to guard against the formation of insoluble albumen, the deliquescent product being then readily soluble in acetic acid, the sodium acetate formed being unobjectionable. In one process the filament is passed through 3% aqueous phenol and in another modification through an alum solution to coagulate the albumen.

According to Silbermann this product is somewhat more brittle than Chardonnet silk, but of a more dazzling white and a higher gloss, which exceeds that of real silk and in its chatoyant nature suggests the Florentine angling lines. The firmness of Vivier silk, reckoned by the same standard, is only equal to 9, while that of mulberry silk is 38, that of Tussah 48. Thiele also states that the firmness of Vivier silk amounts to only about one-fourth that of mulberry silk. According to the statements of Blanc, Vivier silk, observed under the microscope, consists of two single threads, which have great similarity to Tussah silk, yet differ from the latter in their greater thickness, as each of the threads has a diameter of  $20\mu$ , while the single Tussah thread is only  $12\mu$  thick. The Vivier threads are round and appear smooth at the first glance, but on closer examination fine longitudinal stripings appear which result for the fact that the thread is finely grooved lengthwise. The two threads forming the single Vivier thread cling close to each other, without a cementing substance being perceptible. The cross-section of the thread has the form of a fairly regular 8, outer lines of which are slightly wavy. A dividing line between the two threads is also imperceptible microscopically. Yet occasionally along with this double form of the thread, single threads of bean-shaped or elliptical cross-section appear. Blanc traces the double form back to the manner of manufacturing the thread; the spinning-tubes lie very close to each other, the emerging threads cling together and unite immediately. The thread is twisted directly after its production or later, the torsion amounting to about 300 revolutions to the meter. The substance of the Vivier thread is transparent like that of the Chardonnet thread, doubly light-refracting, homogeneous, and contains bubbles which become visible as in Chardonnet thread by treatment with Schweitzer's reagent. The inventor has evidently composed the silk of two threads, in order to make his product as much like natural silk as possible. Yet this clinging of the two threads has the disadvantage that the stiffness of the thread is increased thereby. The Vivier thread is not round—that is, equally pliant from all sides—but flat and twice as long as wide, i.e., inflexible in the direction of greatest thickness. The torsion of the thread also has the tendency to make it stiffer.

**Process of L. Crespin** is designed<sup>1</sup> primarily to use the minimum volume of solvent. To this end, the nitrocellulose is dissolved in a mixture of methyl and ethyl alcohols and ether, to which is added a certain amount of glycerol or castor oil. This collodion is then

1. U.S.P. 820351, 1906, being division of application filed Feb. 4, 1905, Serial No. 244186; E.P. 27565, 1904; F.P. 342077, 1904; abst. J.S.C.I., 1904, 23, 899.

forced through a suitable nozzle into a water-bath, when part of the solvent is dissolved, after which the threads are wound up and the bath treated for the recovery of the contained solvent.

The method preferred is shown in Fig. 134, designed for the manufacture of ribbons and the like, the threads from the forming-nozzle 16 pass around the angular edge 6 of the bath 17 containing the water on its or their way to the winding-roller 18; 19 indicates the main pipe containing the collodion. The water from the bath containing the mixture of ethyl and methyl alcohol is heated to drive off the alcohol, and the latter condensed and collected. To this

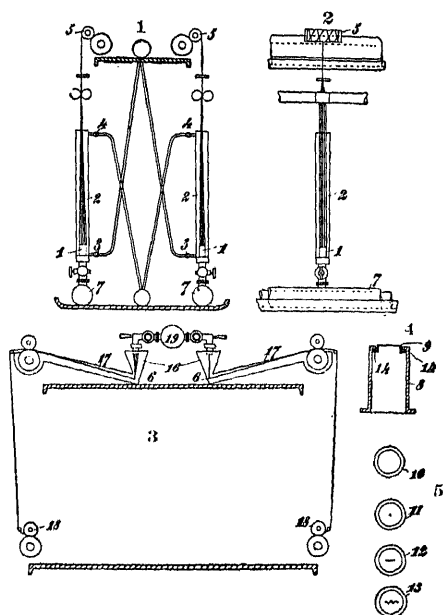


FIG. 134.—The Crespin Process of Making Artificial Silk.

alcohol it only becomes necessary to add again the required weak proportion of sulphuric acid evaporated during the operation and the desired quantities of castor oil, palm oil, or glycerol to obtain a fresh solvent for a further charge of nitrocellulose. As a large portion of the solvent employed may be recovered in this manner, the collodion need not be made very thick. On the contrary, it can be economically made very liquid and fluid, with the result that the heavy pressure previously required to expel the collodion through the nozzles may be very much reduced. In consequence of this the tubes 7 or 19, containing the collodion, may be formed of glass, ebonite, or other suitable material which is inert to, or is incapable of being acted

upon by the collodion. Another advantage of using a very fluid collodion consists in the practicability of employing a forming-nozzle with a series of capillary holes, as indicated in 10. A nozzle may consist of a glass cylinder 8, furnished with a flange, by means of which it may be attached to the cock or tap. At its end is a flanged cap or plate 9, of platinum, which may be perforated with the capillary holes, as shown at 10, or with one larger hole, as at 11, or with straight or undulatory slits, as indicated at 12 and 13 in the same figure, according to whether it is desired to produce artificial silk, horsehair, straw, or ribbons. The joint between the cap 9 and the cylinder 8 is maintained by means of a flexible rubber packing-ring 14, the interior pressure keeping the joint tight.

**Method of M. Denis**<sup>1</sup> differs from that of Crespin in the process of solvent recovery, being otherwise designed both for spinning economically and for regaining the maximum of dissolving fluid. The operation of this process is as follows, and referring to Figs. 135, 136: A suitable liquid at a temperature above the boiling point of ether is introduced into the collector 14, which may be water, and at the commencement of the operation the water fills the collector, and all the cocks on the filament-former being open, the water streams down the tubes 9, carrying with it the collodion filaments issuing from nozzles 6. Ether is but slightly soluble in the water, while the solubility of alcohol at this temperature is about at its maximum. The artificial silk filament will be completely surrounded by hot water as it emerges from the nozzle 6 and be free from contact with air, so that its exterior is not immediately hardened, thereby preventing the imprisonment of solvents in its interior. The ether vapor rises in the tubes 9 into the collector 14 and aids in forcing the heated water through tubes 9. The descending water carries with it the filament and dissolves the alcohol solvent of the collodion. The ether vapor accumulating in the upper part of the collector 14 displaces a quantity of water, which passes through the trap 21a and pipe 21 into the expansion tank 38. In reality the lowering of the level of the liquid in 14 and its rise in 38 are very gradual. The water drops through the tubes 9 into the collectors 19 and is pumped from them through pipe 36, pump 37, and pipe 39 into the expansion tank 38, to again pass through the circuit until sufficiently saturated with alcohol to warrant its being distilled or otherwise treated for the recovery of the alcohol. A definite quantity is withdrawn from the circuit and is replaced by a like quantity of unsaturated water. When the water or other liquid in the collector 14 has reached a suit-

1. U.S.P. 834460, 1906; F.P. 341173, 1904.

ably low level, the float 22 will no longer hold the valve 23 to its seat and the collected ether vapor will be free to pass by pipe 24 to the worm 25, that is kept at a sufficiently low temperature to condense the ether vapor that traverses it, being drawn into the worm by the vacuum pump 27, the residual gas (air) being drawn through the

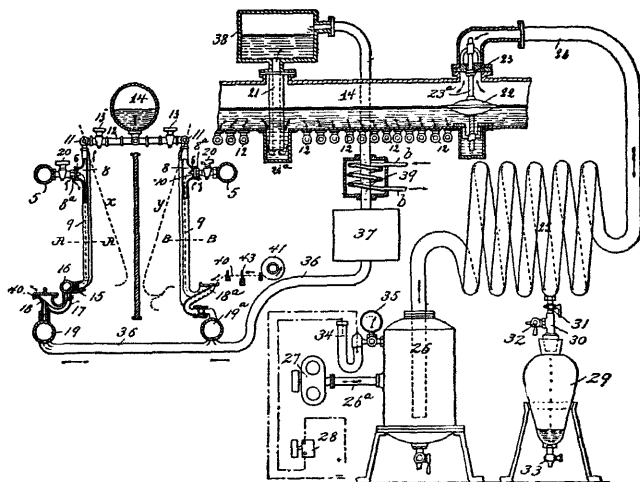


FIG. 135.—The Denis Machine for Producing Threads from Collodion and Recovering the Solvents of Nitrocellulose or Cellulose.

pump. The ether condensate will drop into the glass vessels 29. By closing tap 31 and slowly opening tap 32 the vacuum in the vessels 29 is broken, and the liquid ether condensate can be drawn off through tap 33, which is then closed, as well as tap 32, and the tap 30 slowly opened again to place the glass vessel in operative connec-

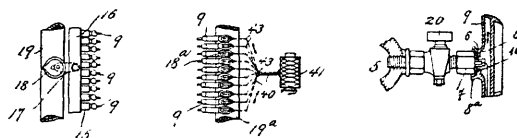


FIG. 136.—The Denis Machine for Producing Threads from Collodion.

tion again with the condenser. As soon as the ether vapor is drawn off from the collector 14 liquid from the expansion-tank 38 will enter the collector, raise the level therein, and close valve 23. The water circulates in a closed cycle and is maintained at the required temperature by passing through chamber or coil *b*, located at any desira-



ble point in the circuit. The water may be replaced by a suitable liquid capable of denitrating the filaments formed.

**P. Cazeneuve** prefers the use of acetone alone as the pyroxylin solvent<sup>1</sup> on account of the ease with which it can be recovered, employing from 2-3 parts solvent to 1 part pyroxylin, and maintaining the solution at 15-20°<sup>2</sup> during the operation of forcing it through the draw-plates. The opaque threads thus produced are unwound from the spools on which they are received from the draw-plates and are exposed, in the form of hanks, for several minutes to an atmosphere of ammonia, at a temperature of 15-25°. This is said to have the effect of rendering them transparent and lustrous. They are next denitrated at a low temperature by means of a solution of ammonium sulphide or hydrosulphide, reagents which have the property, not shared by metallic sulphides, of increasing luster of the filaments, prepared from the solution of nitrocellulose compounds in acetone. Finally the solvent is recovered by the use of a refrigerating apparatus similar to that employed in condensing carbon bisulphide vapors.

**Other Nitrocellulose Filament Processes.** **H. Vittenet**<sup>3</sup> uses acetone instead of an alcohol-ether solvent, and in order to correct the opacity and brittleness of the formed filament due to the rapid evaporation of the acetone solvent, and which the patentee considers is due to the formation of "a hydrate of a mixture of the acetone and nitrocellulose," treats the filament with sulphurous acid<sup>4</sup> after expelling the solvent. It is claimed that the sulphurous acid prevents "hydration" and thus permits of the production of filaments of the desired brilliancy and flexibility. The sulphurous acid is either dissolved in the acetone prior to its employment as a solvent, or a pyroxylin-acetone solution may be directly treated with sulphur dioxide gas, the latter method being preferable. A stream of the gas is allowed to flow into the solution just before spinning, until the requisite amount has been added, the gas decreasing materially the viscosity of the pyroxylin solution. It is claimed the use of sulphurous acid increases the brilliancy and translucency, and aids in the subsequent recovery of the acetone.

**E. Cadoret**,<sup>5</sup> who did considerable work along the lines of coating

1. F.P. 346693, 1904, and First Addition thereto, dated Oct. 26, 1904; the tendency of acetone alone as a solvent is to produce a friable, worthless filament (author).

2. F.P. 350723, 1905, and First Addition thereto, dated Feb. 6, 1905; abst. J.S.C.I., 1905, 24, 194, 331, 799, 967.

3. U.S.P. 828155, 1906; E.P. 1686, 1905; F.P. 350383, 1904; D.R.P. 171639, 1905.

4. U.S.P. 842125, 1907.

5. Not Cardaret; E.P. 8558, 1894; 12451, 1896; Cadoret and E. Delgrade,

textiles with nitrocellulose,<sup>1</sup> combines both glue and pyroxylin through the intermediary of their mutual solvent, acetic acid. E. Bronnert and T. Schlumberger<sup>2</sup> economize on solvent by the use of strong ethyl alcohol to which is added citric, oxalic, tartaric, lactic or levulinic acids, to increase the solubility, avoiding the danger of drying moist nitrocellulose by incorporating with it small amounts of calcium or magnesium chlorides. A. Loncle and H. Chartrey<sup>3</sup> use a mixture of ether and methyl alcohol together with 1% acetone for the solvent, and dry the formed thread by simple exposure in the atmosphere for about seventeen hours. E. Oberle and H. Newbold<sup>4</sup> spin the filament by means of reduced pressure and suction instead of forcing the solution through the spinnerets by pressure. Nitrostarch combined with cellulose nitrate through the solvent methyl alcohol and acetone has been described<sup>5</sup> as a suitable material for filament formation. A. Petit<sup>6</sup> and independently P. Germain<sup>7</sup> describe

E.P. 21485, 1892; Vogel and Cadoret, *Lehnes Farb. Ztg.*, 1897, 8, 7; Cadoret, *Rev. Ind.*, 1894, 25, 64; *Mon. Teint.*, 1894, 38, 5; *Ind. Text.*, 1894, 10, 111. See P. Jenny, D.R.P. 98602, 1897.

1. See *Textiloid*, F.P. 256854, 1896; abst. J.S.C.I., 1893, 12, 779; 1895, 14, 569; 1897, 16, 449; 1898, 17, 164. *Muster Ztg.*, 1897, 46, 450.

2. E.P. 6858, 1896; abst. J.S.C.I., 1897, 16, 355; see Eder (Ber., 1880, 13, 1841). The product obtained by the Vereinigte Kunstseidenfabriken Frankfurt by spinning a solution of acid cellulose in caustic soda and precipitating the thread as it comes out of the capillaries by means of an acid bath, appears to be only capable of yielding good results when 10 parts of cotton are mixed with 100 parts of sulphuric acid of sp.gr. 1.55, the mass thrown into water and the precipitated acid cellulose, after washing, dissolved in 100 parts of caustic soda solution, sp.gr. 1.12.

3. *Mon. teint.*, 41, 66; In the patented process of E. Huwart (F.P. 383555, 1907) nitrocellulose is dissolved in substances belonging to the class of acetals of the fatty series or in their chlorine or bromine derivatives, or in the aldehydes or ethers derived from these acetals. This class of substances is characterized by the presence of an aldehyde radical combined with two similar or different alkyl radicals, as for example in the compounds,  $\text{CH}_3(\text{OCH}_3)_2$  and  $\text{C}_2\text{H}_5(\text{OCH}_3)(\text{OC}_2\text{H}_5)$ . These compounds may be employed alone or in methyl or ethyl alcohol solution.

4. *Leip. Farb. Ztg.*, 1897, 311; *Muster Z.*, 1897, 46, 311. F.P. 258257, 1896; see Heberlein & Co., E.P. 3861, 1901; "Production of Silky Gloss upon Cotton Yarn by Impregnating with Collodion;" also *Text. Col.*, 1897, 19, 229; Grandquist, E.P. 23729, 1899.

5. G. Arnold, A. Fox, A. Scott and H. Roberts (E.P. 3450, 1906); G. Gorrand (E.P. 6166, 1906) prepares the collodion from which the threads are spun from a solution of nitrocellulose in acetone, amyl alcohol and acetic acid, ammonium sulphide being the denitrifier; C. Brodbeck (E.P. 18119, 1890) puts a final coating of silk fibroin on the filament. For finishing artificial silk, see Hubner, E.P. 19166, 1910.

6. Not Petit; U.S.P. 665975, 1901; E.P. 15343, 1900; best results are said to have been obtained by using dry nitrocellulose 100; india-rubber solution 7; stannous chloride 5; the solvent being benzene. Such a formula is impossible of combination.

7. F.P. 355016, 1905. In F.P. 360395, 1905, Germain prepares a homogeneous paste by dissolving nitrocellulose, celluloid, and naphthalene in acetone, and adding to the solution powdered barium sulphate. The paste is then spun into threads, which are at once immersed in dilute sulphuric acid. This removes the acetone, which may be recovered for further use. The excess of acid remaining in the threads is neutralized by treatment with barium hydroxide solution. Other means, such as heating, etc., may be employed for the removal of the acetone. The threads are not denitrated, and they may be redissolved when desired, the barium sulphate, of course, remaining undissolved.

combinations of pyroxylin with caoutchouc, acetone oil being the solvent, the process of E. de la Grange being substantially the same.<sup>1</sup>

A. Lumière and Sons<sup>2</sup> believe in filtering the pyroxylin solution when very fluid, subsequently concentrating (when necessary) by partial vacuum distillation.<sup>3</sup> Their method of "collodion filament" manufacture<sup>4</sup> comprises a chamber adapted to be traversed by the filaments after leaving the discharge nozzle and containing a spongy material intended to be separated with alcohol, in combination with a rotatable receptacle designed to contain a coagulating substance and into which the filament falls by gravity from the chamber, and is coiled by the rotation of the receptacle about an axis non-coincident with that of the filament.

In addition to improvements in spinning methods (described elsewhere), R. Strehlenert<sup>5</sup> has made many minor suggestions looking toward simplifying the formation of nitrocellulose filaments, especially from a mechanical point of view. J. Duquesnoy<sup>6</sup> dissolves the pyroxylin in a mixture of equal volumes of acetone, glacial acetic acid and amyl alcohol, and expresses the solution from a capillary orifice projecting into the external atmosphere and without the interposition of a fluid coagulating medium. In the process of J. Sauverzac<sup>7</sup> the nitrocellulose is dissolved in the solution of a metallic chloride

1. E.P. 16332, 1900; Sw.P. 22680. For pumps for supplying collodions to filters and drawing apparatus, see L. Desmarais, G. Morane and M. Henis, E.P. 6783, 1905; F.P. 342655, 1904; abst. J.S.C.I., 1901, **23**, 933.

2. F.P. 361324, 1905. Their process of preparing "collodion of high standard" for artificial silk manufacture capable of immediate drawing into threads, consists in dissolving thoroughly air-dried nitrocellulose in a mixture of methyl and ethyl alcohol and ether, then distilling the filtered solution to half its volume. For 300 k. cellulose, 200 l. each of methyl and ethyl alcohols, and 1,600 l. ether, are employed. Distillation is continued until the ether content is reduced to 600 l.

3. F.P. 361324, 1905, their fluid collodion being prepared by dissolving 300 parts nitrocellulose in 200 parts methyl alcohol, 200 parts ethyl alcohol, and 1,600 parts ether. Owing to the excess of ether, this collodion is very fluid, and can be easily filtered under a slight pressure. The collodion is then distilled in a vessel provided with stirrers, until 1,000 parts ether have been driven off and condensed for future use. The concentrated collodion is cooled, and having already been filtered and freed from air while in the dilute condition, it can be directly stored in closed vessels and is then ready for spinning.

For the filtration of collodion (F.P. 361329, 1905) for the preparation of artificial silk, a continuous roll of filtering medium is provided outside the press. A portion of the fabric is clamped tightly over the perforated support by means of a screw-head, and the collodion is admitted from below under pressure, through a pipe provided with a stopcock. When the filtering surface has become clogged, the stopcock is closed, the conduit for filtered solution is also closed, the screw raised slightly, and a new filtering surface is pulled through from the roll, and is clamped down ready for use.

4. E.P. 89A, 1907.

5. Abst. J.S.C.I., 1897, **16**, 533, 907; 1899, **18**, 579; 1902, **21**, 969; 1903, **22**, 92, 1345.

6. U.S.P. 663739, 1900; E.P. 8799, 1900.

7. F.P. 402950, 1908; see also E.P. 1858, 1896; abst. J.S.C.I., 1897, **16**, 335.

in alcohol. A solution of 10 gm. of aluminum chloride in 100 cc. of alcohol dissolves 50 gm. of nitrocellulose, and the mixture may be diluted with as much as 80% of water. The threads spun from this solution are said to be very supple and elastic. H. Woltercek<sup>1</sup> passes cotton thread of varying degrees of fineness, the luster of which may be increased by previous mercerization, through a nitrocellulose solution, subsequently denitrating in the usual manner.

**Denitration of Cellulose Nitrate.** The necessity of denitrating nitrocellulose artificial silks in order to reduce their inflammability is perhaps the weakest point in the process, and the point which is of most importance as standing in the way of further development. All forms of cellulose with the exception of the acetate, irrespective of their treatments in the formation of filaments, are eventually regenerated to cellulose, or nearly so, before becoming merchantable products. It appears that in 1878<sup>2</sup>—before the artificial silk industry had commenced—the disadvantage of the inflammability of the cellulose nitrates was appreciated, as witnessed by the publication of methods of denitration. In the earliest process of which the author is aware the dried pyroxylin was deoxidized by digestion with sulphurous anhydride under pressure, with sodium bisulphite solution containing phosphoric acid or with sodium thiosulphate solution. In 1900 L. Vignon<sup>3</sup> studied the reduction of nitrocelluloses by the action of ferrous chloride and found that when 20 cc. sat. aq. sol. of ferrous chloride was boiled for ten minutes with 1 gm. of a cellulose nitrate, there was liberation of nitric oxide, and it was shown that although the nitro groups were eliminated the aldehydic groups were left intact.<sup>4</sup> The next year H. Richter,<sup>5</sup> as the result of exhaust-

1. E.P. 3898, 1898; E. Breuer (D.R.P. 55293, 1890) has devised a novel process for producing colored nitrocellulose threads by coating a roller of sheet metal or other material with a layer of pyroxylin, then with dissolved glue, proceeding alternately until the required thickness is obtained. The roller is then put in a screw-cutting lathe, and the coating cut through spirally, thus furnishing a continuous thread. For the artificial silk process of L. Lederer in which an acetone solution of nitrocellulose is mixed with an acetylene tetrachloride solution of cellulose acetate, see E.P. 11625, 1909.

2. P. Magnier and L. Doerflinger, E.P. 4711, 1878; see also W. Green, E.P. 9879, 1889; "Denitration of Pyroxylin," *Chem. Zeit.*, 1905, **29**, 420.

3. C.R., 1900, **131** (12) 530; *Bull. Soc. Chim.*, 1901, (3), **25**, 130.

4. He found that when cellulose and oxycellulose of maximum and minimum nitration (13.5, 13.9, 8.19, and 8.36% nitrogen respectively) were treated with ferrous chloride in boiling aqueous solution, the products formed were oxycelluloses with a cupric reduction equivalent to that of an oxycellulose prepared directly by the action of chloric acid. Conversely, where ammonium sulphide was used as the denitrifier, and at 35–40°, the products obtained were without action on copper solutions. This is to be construed as indicating that nitrated cellulose should be regarded as a derivative of oxycellulose.

5. E.P. 12695, 1901; where cupric salts are used, the fluid after denitration contains cuprous salts, and by the addition of common salt and conducting sulphur dioxide through the solution, cupric salts are again formed.

ive studies on the denitration of artificial silk, obtained patent protection for a method in which the nitrated filament is treated in an acid solution of a metallic salt which is in a lower state of oxidation and is capable of passing to a higher state of oxidation. Suitable salts found are cuprous chloride, cuprous oxychloride, ferrous, manganous, chromous, antimonous, stannous, mercurous or cobaltous salts, ferrocyanides and nitroprussides. With the use of cuprous salts, hydrochloric acid is advantageous. In order to facilitate and render more complete the denitration, certain agents may be added which will cause the nitrocellulose to swell, such as alcohol, ether, ketones, glycerol, epichlorhydrin, turpentine, and solutions of caoutchouc and glue. Substances may also be added with advantage which dissolve the salts employed, such as alkaline thiosulphates, ammonium sulphate, and the chlorides of the alkalis and alkaline earths, or of iron, zinc or manganese. Cuprous chloride and oxychloride, being difficultly soluble, may be dissolved in acid and partially neutralized with ammonia, or dissolved in ammonia and neutralized with acid. Where large amounts are treated, methods for drawing off the nitrogen oxides and recovering them are described and may be useful, but it is customary where small amounts are denitrated at a time to make no effort to recover the liberated nitrogen.<sup>1</sup> Other denitrating agents which have been employed are ammonium nitrate,<sup>2</sup>

1. In Chem. Ztg., 1909, **33**, 174, E. Bindschedler claims priority through his deposition of June 15, 1908, over Coulier's Belg. P. of Sept. 28, 1908, for method of recovering sulphur, nitrites, ammonia, alkalis, and alkaline earths from baths used in denitrating cellulose nitrates. P. Heermann (Mitt. kgl. Materialprüfungsamt., 1910, **28**, 227) reports that milky or chalk-like spots found to develop in a consignment of nitrocellulose artificial silk gradually increased until the whole skein was attacked, the fiber becoming brittle and worthless. The aqueous extract of the damaged parts was strongly acid, and gave a precipitate of barium sulphate equivalent to 1.03% of sulphuric anhydride. The undamaged parts (also a sample of the same silk not denitrated) gave an aqueous extract which was neutral and did not give a precipitate of barium sulphate, but sulphuric acid was found after heating the silk with caustic soda. The undamaged portion heated in an air-bath to 120-130°, quickly became acid and on longer heating at 125-130° partly carbonized. Well-made nitrocellulose artificial silk showed no trace of carbonizing when heated to 135-140°, and the aqueous extract showed no trace of sulphuric acid; only a trace of the acid was detected after heating with caustic soda. The trouble is therefore ascribed to the presence in the raw nitrocellulose of sulphuric acid, probably existing as a cellulose sulphuric ester, which was not removed on denitrating and which decomposed gradually on keeping the silk, liberating sulphuric acid.

2. Process of R. Valette, E.P. 20637, 1904; F.P. 344660, 1904; abst. J.S.C.I., 1904, **23**, 1212. Serret (F.P. 369170) denitrates with aluminum chloride. (C. Dow (D.R.P. 153671) seeks to still further reduce danger of inflammability by treatment of the filament with formaldehyde after denitration, but if the latter process is properly conducted, further treatment is unnecessary. By the process of the Soc. Anon. Hongroise pour la Fabr. de la Soie de Chardonnet (F.P. 410652, 1909) solutions of alkali or alkaline earth sulphhydrate which have been used for the denitration of nitrocellulose, and which contain sulphides and nitrites, are added to excess of mineral acid (*e.g.*, the acid which has been used for the nitra-

ferrous chloride,<sup>1</sup> ferrous chloride in alcohol,<sup>2</sup> formaldehyde,<sup>3</sup> and sulphocarbonates,<sup>4</sup> but none have proven as satisfactory as the sulphides and hydrosulphides, although the latter vary greatly in their action, depending on the metal in combination.<sup>5</sup> Thus the calcium compounds have a tendency to harden and weaken the filament, the magnesium salt works rapidly and tenders the thread the least, while the ammonium compounds require great care in handling, and are comparatively costly. Although P. Cazeneuve<sup>6</sup> has described a process of denitrating pyroxylin by treating its acetone solution with metallic sulphides before formation into filaments, the threads are usually wound on to bobbins and denitrated in this manner. In one method<sup>7</sup> the bobbins of artificial silk are arranged

tion); the hydrogen sulphide and the nitrous anhydride thus evolved interact, sulphur being precipitated, and nitric oxide set free.

1. Bechamp, *Ann. Chim. Phys.*, 1863, (3), 68, 462.
2. Chardonnet, First Addition, dated Mar. 3, 1897, to F.P. 231230, 1893.
3. Knöfler, F.P. 247855, 1895; D.R.P. 88556, 1894.
4. See D. Woodman, J.A.C.S., 1892, **14**, 112, on denitration of celluloid to cellulose for production of incandescent electric light filaments. According to A. Dulitz (*Chem. Ztg.*, 1910, **34**, 989) it is impossible to obtain a product absolutely free from residual traces of nitrogen without the destruction of the threads. For practical purposes it is sufficient to prepare a denitrated silk containing 0.05% of nitrogen, provided the distribution of the denitrating action be absolutely uniform. Uniform denitration depends on uniformity in composition of the nitrocellulose threads and their uniform shrinkage; also on uniform moisture in the threads which are suspended in the denitrating bath. The quantity of denitrating liquid per k. of nitrocellulose must always be constant and the composition, the initial temperature and the changes in temperature of the bath during the process must be accurately controlled. The time of action of the denitrating bath is of the highest importance. The titration of the bath and the examination of the threads with the polarizing microscope are not very satisfactory guides in judging the end-point of the denitration process. In order to be quite certain, the threads should be treated rather longer than appears to be strictly necessary. Nevertheless it must always be borne in mind that a prolongation of the treatment involves a loss of strength of the product. Any addition of substances, such as resins or oils, to the collodion has an unfavorable influence on the denitration and necessitates a longer treatment, with consequent loss of strength. The addition of acids with a view to reducing the viscosity of the collodion also detracts from the quality of the finished silk and appears to promote the formation of oxycellulose. The author points out that whereas fresh solutions of hydrosulphides attack the denitrated threads but slightly at 40°, a solution which has already been used for denitration attacks them powerfully. He believes that the nitric acid groups split off from the cellulose during denitration are capable of inducing a secondary oxidation of the cellulose, part of which then enters into solution in the bath. The hydrosulphides alone are not sufficient to fix these nitric groups in such way as to avoid injury to the cellulose, and various other substances are generally added. The concentration of the denitrating bath should be fairly high.

5. Bechamp, l.c.; Blondeau, *Ann. Chim. Phys.*, 1863, (3), 68, 462.

6. First Addition, dated Oct. 26, 1901, to F.P. 346693, 1904; abst. J.S.C.I., 1905, **24**, 194. By this process it is stated that a solution in acetone of "true amino-nitrocellulose" is obtained, which is specially adapted to the direct formation of threads.

7. Process of H. Diamanti, P. Loisel and H. Champin, F.P. 378143, 1906; see also H. Diamanti, F.P. 17460, 1907; abst. J.S.C.I., 1907, **26**, 1136; in L. Bergier's process (F.P. 349134, 1904) the threads are denitrated by immersion for some

vertically in a wooden frame which can be inserted as a whole inside an airtight vat. This vat, which may be made of wood or stoneware, is provided with means for placing it in communication with a tank containing the denitrating solution, and also with an exhausting apparatus. A number of vats are worked in series, each being connected to its immediate neighbors. The vats are first exhausted, and the denitrating solution then circulated through the whole series, care being taken that the fresh solution always comes in contact with bobbins which have already been almost completely denitrated.

The preferred strength of sulphide depends upon the metal attached, and with ammonium sulphide with the amount of sulphur, it having been found that the yellow or polysulphides are much more energetic denitrifiers than the simpler sulphides. For this reason it is indicated to add sulphur either direct to ammonium sulphide prepared by saturating aqueous ammonia with hydrogen sulphide, or else by exposing the sulphide to the light to polymerize. The denitration may be accelerated, according to G. Corrand<sup>1</sup> by adding a few drops of acetic acid to the nitrocellulose solution before spinning, where ammonium sulphhydrate is employed. The correct strength of the denitrating bath may be determined by (a) the loss of solubility of the treated thread in cellulose nitrate solvents, (b) determination of nitrogen in thread, (c) and examination under the microscope. With the latter procedure, if the sulphide is unduly concentrated, the too vigorous action may be recognized by the appearance of the threads, which will be dull and lusterless, occasionally corroded, and free from color formation under the polariscope. The weakness of the sulphide is readily determined by the solubility of the (supposedly) denitrated thread in a mixture of alcohol, ether and acetone, equal parts of each. Theoretically 8 molecules of hydrogen sulphide are required per molecule tetranitrocellulose, but experience has shown that 4 molecules of sulphide, with proper precautions, are sufficient to reduce the nitrogen contents under 0.25%, and usually from 0.14–0.18%. With but traces of nitrogen remaining, examination with diphenylamine in concentrated sulphuric acid, especially when made against control samples with definite amounts of nitrogen therein, admit of quite accurate approximations being made. The denitrated filament, like cellulose, hours in a solution of cuprous chloride acidified with HCl, and at a temperature of 60°, all traces of copper being subsequently removed by treatment with dilute hydrochloric acid, followed by thorough washing.

1. F.P. 354424, 1905; E.P. 6166, 1906; in the process of the Soc. Anonyme de Soie Artif. de Tubize (F.P. 358987, 1905) the silk is allowed to remain on the bobbin during the denitration and subsequent bleaching, thus obviating twisting, dividing and making into skeins.

is permeable by water, and Germain<sup>1</sup> proposes to overcome this by dipping the threads after denitration into a weak pyroxylin lacquer, just sufficient to render the filaments impermeable, but insufficient to materially raise the inflammability. Various inventors, e.g., R. Valette,<sup>2</sup> D. Bachrach,<sup>3</sup> R. Langhans,<sup>4</sup> L. Bethisy,<sup>5</sup> A. Plaissetty,<sup>6</sup> Du Vivier,<sup>7</sup> Cadoret,<sup>8</sup> Lehner<sup>9</sup> and others<sup>10</sup> have endeavored to reduce the inflammability by adding certain metallic salts without denitrating the nitrocellulose, but as yet without satisfactory results. Attempts have also been made to reduce the tendency of the fiber to weaken when wetted with water by the use of partially water-soluble sulphonated vegetable oils, especially corn and castor.

The fiber upon emerging from the denitrating bath is a dirty, pale yellow, and has therefore to be subjected to a bleaching process before being offered for sale. A small amount of bleaching powder and hydrochloric acid is generally used, the quantities for Chardonnet silk being stated as bleaching powder 4, commercial hydrochloric acid 8, and artificial silk 16. The bleached skeins are carefully washed in cold water until all free chlorine is removed and either directly dried or subjected to an intermediate softening process with Turkey-

1. D.R.P. 160396, 1905; see also Compagnie de la Soie de Beaujeu, D.R.P. 217128, 1907.

2. E.P. 20637, 1901, using ammonium nitrate. See also "Decreasing Inflammability" in Chapter XIV.

3. U.S.P. 791581, 1905; E.P. 2339, 1901; certain volatile, non-aqueous liquid silicates such as methyl, ethyl and amyl silicates, the so-called "silicic ethers" being used. In this and the following processes the thread is dipped in a concentrated solution of the salt or ester and after thorough impregnation, dried under tension to increase the luster.

4. U.S.P. 571530, 1896, phosphosulphuric and phosphoric acids being claimed.

5. U.S.P. 625313, 1899, zinc chloride and gelatin being added; in the method of A. Dubose (Bull. Rouen, 1909, Sealed Document, No. 530; Chem. Zeit., 1905, 29, 822; Bull. Rouen, 1905, 33, 318; 1908, 36, 272; Muster Ztg., 1905, 53, 19) tannin is added to the solvent used in making Chardonnet silk. Thus the spun fiber contains tannin, and a reducing substance is employed for the purpose of denitration, instead of ammonium sulphide, the base of this reducing substance uniting with the tannin to form an insoluble compound. Before denitrating, it is recommended that the fiber be passed through Turkey red oil. Substances which are recommended as reducers are sulphides of magnesium, aluminum, antimony, tin, and silicon; magnesium, calcium, or aluminum hydrosulphides or stannites, and tin chlorides.

6. E.P. 9087, 1900, anhydrous aluminum chloride or nitrate being applied either directly to the nitrocellulose or added with a solvent.

7. Rev. Industrielle, 1890, 194; D.R.P. 52977, 1889.

8. F.P. 256854, 1896. E. Müller (D.R.P. 222777, 1909) protects the silk gloss produced on fabrics by goffering, from the injurious action of moisture by treatment with nitrocellulose solutions, employing epichlorhydrin as the nitrocellulose solvent.

9. D.R.P. 55949, 1889; 58508, 1890; 82555, 1894.

10. In the process of the Soc. Anon. pour l'Étude Ind. de la Soie Serret, F.P. 369170, 1906, the fiber is impregnated with a solution of aluminum chloride, while with Soc. pour la fabrication en Italie de la soie Artif. par le procédé de Chardonnet, F.P. 367803, 1906, calcium or magnesium chloride is employed. See Chardonnet, Ind. Text., 1893, 9, 175.



red oil, sulphonated lard oil or similar material to counteract the tendency to harshness produced by the bleaching process. The final product has a white color, and this may be intensified by the addition of a trace of methyl violet, indigo, or ultramarine.

**Solvent Recovery.** The recovery of the ether and alcohol contained in the air of artificial silk factories has been many times proposed, but is extremely difficult on account of the high degree to which the vapors are diluted with air, and the mechanical equipment required to take care of the millions of cubic feet of air circulating in a properly ventilated factory of any considerable magnitude. The methods proposed previous to 1904 have all proven unsuccessful from an economical point of view, and need not be mentioned here. In one method largely practiced<sup>1</sup> the air containing ether and alcohol vapor is passed through absorption towers containing sulphuric acid, the latter being distilled in vacuum to recover the alcohol and ether. It was found, however,<sup>2</sup> that by mixing the acid with 1 or 2 molecules of water, the tendency toward formation of ethyl sulphuric acid was diminished, and loss of ether from this source obviated.<sup>3</sup> By varying the concentration of the acid, the speed with which the air passes through it, and the temperature of the condensing chambers, the by-products formed—which at first militated greatly against the process—have been materially reduced in amount. In the method of O. Buequet<sup>4</sup> a liquid fat or fatty acid, either alone or mixed with an oil of low solidifying point, is used as an absorbent of the vapors of the volatile solvents. When the absorbent is saturated, the volatile solvent is recovered by distillation under diminished pressure. In the process of A. de Chardonnet, patented in 1906,<sup>5</sup> the air containing the vapors is passed through a series of towers

1. J.S.C.I., 1906, 25, 71.

2. F.P. 350290, 1904. In the process of Fabrique de Soie Artif. de Tubize, F.P. 401262, 1908, in place of sulphuric acid 66° Bé. it is proposed to use acid of no more than 62° Bé., claiming that the absorptive power of the more dilute acid is sufficient, and the reconcentration which is required from time to time may be carried out in leaden vessels instead of the platinum ones employed for the 66° Bé. strength. In Dervain's process (F.P. 350298, 1904) the spinning operation is conducted in closed chambers with the primary object of limiting the amount of air which it is necessary to treat, and thus diminish the amount of sulphuric acid required for absorption.

3. In U.S.P. 712406, F. DuPont, the material carrying the alcohol-ether vapor is immersed in alcohol and a gas caused to pass through it, carrying off the ether.

4. D.R.P. 196699, 1907.

5. D.R.P. 207554, 1907; F.P. 377673, 1906, and First Addition thereto, dated July 27, 1906; abst. J.S.C.I., 1907, 26, 1088. In D.R.P. 207554 the method consists in bringing the alcohol and ether intimately into contact with the higher-boiling members of the fatty acid alcohols, such as propyl, butyl, amyl, and other alcohols, as well as their derivatives such as butyl acetate, butyric acid, etc., in general also the so-called last runnings of the alcohol distillation process, and then distilling off from the resulting solution the compounds named.

or chambers into which amyl alcohol or other high boiling alcohols are sprayed. The vapors are absorbed by the alcohol, which is passed through the series of towers in the opposite direction to the air, the weak solution obtained in the last tower of the series being sprayed into the next and so on. The alcohol or ether is recovered from the strong solution obtained in the first tower by distillation either conducted at the atmospheric pressure by heat, or in the cold under reduced pressure. The residue left in the still is used over again. In the manufacture of artificial silk, the alcohol and ether which are given off at different stages in the process are either recovered separately or are allowed to mix and the alcohol recovered first by passing the air through a similar train of apparatus into which water or water containing a little alcohol or calcium chloride is sprayed.

The essence of H. Diamanti's method is to collect<sup>1</sup> the vapors given off by the threads by first causing these latter, immediately on issuing from the draw plates, to enter a passage traversed by a suction current of air moving in the opposite direction to the movement of the threads, the latter being then rolled upon spools in an almost air-tight casing and further treated by means of a controllable blowing of air on each spool and a suction device for removing the vapors, the air thus forced in being fresh air, dried artificially or not, or purified air previously used in the process.

In the process of S. Douge<sup>2</sup> the first step is to concentrate the mixture of air and vapor by successive treatments in centrifugal separators, or similar means, returning the vapor-free air to the factory, and the air rich in vapor is then subjected to a selected treatment of absorption, distillation, etc. The specific gravities of air and the vapors of the usual solvents (ether, chloroform, carbon bisulphide) being so different, the method of treatment is said to give very excellent results, the difference in cost between that for treating the whole bulk of air with absorbent and that for first "separating" and then treating the concentrated mixture with absorbent, being much in favor of the newer method.

In a still more recent process<sup>3</sup> the mixture of vapor and air is compressed and cooled and passed through an apparatus in which progressive refrigeration is possible. The compressed and cooled mixed gases are further cooled by permitting them to expand, and are

1. E.P. 5020, 1907; see solvent recovery apparatus of M. Denis (E.P. 4534, 1905; F.P. 341173, 1904).

2. E.P. 1595, 1907.

3. Soc. "L'Air Liquide" (Soc. anon. pour l'Etude et l'Exploit. des Proc. G. Claude), F.P. 397791, 1908, and First Addition thereto, dated July 16, 1909; F.P. 413571, 1909.

then used as cooling agents for a further quantity of the compressed gases. By this arrangement very low temperatures may be reached, but it is essential that the temperature should not be such as would cause the separated liquids to freeze and block the apparatus.

In the procedure of C. Crepelle-Fontaine<sup>1</sup> the air containing the vapors of alcohol or ether is withdrawn from the working place by a fan and is discharged into the base of a column, divided by horizontal partitions into sections, each of which is provided with a bubbling weir or hood and an overflow pipe. The air passes up the column and bubbles through an acid or other suitable absorbing liquid, which flows down the column from an overhead supply tank. The liquid flows from the bottom of the column through a cooler, where its temperature is reduced, to a well from which it is pumped back into the overhead tank. The column is provided with thermometers, as it is necessary for the successful recovery of the vapors to maintain the column and washing liquid at a suitably low temperature. It is claimed<sup>2</sup> that by the use of a machine analogous to those of the Linde, Lourniet, or Pietet types, whereby by combined refrigeration and compression, the volatile vapors may be condensed and subsequently separated by centrifugal or other means from the atmosphere of the workshop. In a recent paper read before the French Academy on this subject, a process for solvent recovery was described and said to be remarkably economical and satisfactory from the yield obtained. The method consists in compressing the air containing the volatile vapors under 4 atmospheres, passing it up a large tower, and gradually cooling from the bottom until at the top a temperature near that of liquid air is reached. By this means the water is eliminated at first, thus obviating the difficulty of freezing in the pump. The yield was stated to be from 90–95% of the volatile vapors in the air.<sup>3</sup>

1. F.P. 396664, 1908; 401182, 1909; U.S.P. 951067, 1910; E.P. 2100, 1909; abst. J.S.C.I., 1909, 28, 597.

2. Soc. Anon. pour la Fabrication de la Soie de Chardonnet, F.P. 387051, 1908.

3. The Soc. pour la Fabr. en Italie de la Soie Artif. par le Procédé de Chardonnet, in F.P. 371985, 1906, displace the volatile solvent by a current of steam, which is condensed in a cooling or condensing medium. Their F.P. 367803, Addition thereto, dated Mar. 11, 1907, describe, that according to the principal patent, the products obtained by forcing a collodion solution through an orifice, are washed either by pure water, or by an aqueous solution of some metallic salt, which is led through a perforated pipe placed above the bobbins or rollers on which the product is being wound. In the addition an apparatus is described which is applicable to rollers or bobbins which are driven by a rotating cylinder with which they are in contact. Around the lower half of the driving cylinder, a hemi-cylindrical trough is arranged, into which the washing liquor is led at one end by a pipe which almost touches the bottom, leaving by an overflow pipe at the other end of the trough. The overflowing liquor is run either into the next trough if several are being used, or into the distilling apparatus. When the machine is working, the rapidly rotating cylinder carries with it some

In the recently protected process of A. de Chardonnet for the collection and recovery of volatile solvents in the preparation of artificial filaments, etc., from collodion,<sup>1</sup> the concentration of the vapors of the solvent in the air must be kept as high as possible. The spinning apparatus is enclosed in a glass case which is opened only when necessary. The ordinary rail carrying the spinnerets is replaced by a revolving plate having spinnerets arranged in the form of a circle. Each plate is provided with a control tap and a special filter, and when the spinning from any particular plate is interrupted a tight-fitting globe is placed over the plate to prevent loss of solvent. The filaments pass up through guide-forks onto the bobbins, which, when full, are placed in the lower part of the casing until all the ether and most of the alcohol have evaporated. The unwinding of the bobbins is effected after immersing them in water in order to collect some of the alcohol, and the spindle of the bobbin during the unwinding process is surrounded by a light metal cylinder against which the dilute alcohol is thrown by centrifugal force and collected. For the absorption of the ether and alcohol vapors, amyl alcohol (or its homologues) is employed, as described, i.e., in a vessel containing plates. The vapors of the amyl alcohol carried off from the first absorption vessel by the issuing air are absorbed in a second plate-apparatus charged with dilute ethyl alcohol, which may be obtained from the bobbins. The vapors carried off from the second vessel are absorbed in a third, which is charged with water. The alcohol and ether absorbed by the amyl alcohol are recovered by rectification in a rectifying plate-column, and the alcohol from the second and third absorption vessels is recovered in a second rectifying column.

of the washing liquid which is thus brought into intimate contact with the product which is being wound on the bobbins. It becomes charged with the mixture of alcohol and ether and then falls back into the trough. G. Claude (C.R., 1909, 119, 780) computes that one million francs' worth of volatile liquids are lost annually in the artificial silk industry alone, and recommends the method of recovery by freezing, using the same principle as that by which liquid air is made. To get rid of the water vapor the air is first cooled by passing through refrigerators full of obstructions. The air is then cooled to  $-90^{\circ}$ , when the vapor tension of alcohol and ether are negligible. He states it is possible to treat 20 cu.m. of air per horse power per hour and recover 90% of the vapors.

1. F.P. 413359, 1909; cf. J.S.C.I., 1907, 26, 1088. The process of the Fab. de Soie artificielle de Tubize (F.P. 11729, 1910; F.P. 412887, 1909; abstr. J.S.C.I., 1910, 29, 1004) relates to the arrangement of the walls of the cabinet, which completely encloses the filament-producing apparatus. The front of the cabinet is composed of two superposed counterbalanced frames, dividing the wall into an upper and a lower accessible zone, corresponding with the position of the essential parts of the apparatus, i.e., the capillaries below and the winding drums above. According to J. Smith, H. L. Mitchell, W. H. Askham, and H. Hey (F.P. 18605, 1909) the air containing the vapor of the solvent is drawn into the cylinder of a suitable pump and at each stroke of the pump a quantity of absorbing oil is

The patent of A. Collard<sup>1</sup> relates to apparatus for the recovery of ether, acetone, alcohol and similar vapors, by bringing the air into intimate contact with a suitable absorbing liquid. In one form, the apparatus comprises a scrubbing column and a gas-washer; the absorbing liquid is sprayed with the air into the lower part of the scrubbing column, a supply of pure absorbing liquid is admitted at the top of the column, and a third supply of pure liquid is admitted to the washer. Distilling, rectifying and condensing apparatus are also provided for separating the ether, acetone, etc., from the absorbing liquid.

A method which is stated<sup>2</sup> to have proved successful since 1906 in a Hungarian artificial silk factory, consists in operating the reels on which the artificial silk is wound by means of a roller on to which water is sprinkled. In this way the solvent is washed out of the wet fibers, the supply of water being so regulated that the liquid flowing off the roller contains about 14% of ether-alcohol, which is subsequently recovered by distillation.

**"Cuprammonium Silks"**<sup>3</sup> is the general term applied to those artificial filaments which result from dissolving cellulose in an ammoniacal copper solution, forming filaments therefrom, and regenerating cellulose from the copper-containing compound. The first patent connected with this process was taken out in France by L. Depeissis in 1890,<sup>4</sup> but on account of the death of the inventor before the final acceptance of the patent,<sup>5</sup> according to the French law of that date, the patent was never published, the only record of its contents being a synopsis appearing in a French publication. Being abandoned by the inventor's death, the original is unavailable for reference. Nothing more was heard of the process until 1897, when H. Pauly<sup>6</sup> patented a process in which the essentials are anticipated by the pre-

drawn into the cylinder along with the vapor-laden air. These become intimately mixed in the cylinder and the solvent is absorbed by the oil. Oil and air are discharged from the pump, the air, now freed from the solvent, escapes and the oil containing the solvent is collected in a reservoir and subsequently distilled to regain the solvent for use.

1. F.P. 410555, 1909; see also F.P. 413571, 1909.

2. A. Vajdasy, *Vegyészeti Lapok*, Budapest, 1909, 4, 103. *Chem. Zeit.*, 1910, 34, Rep., 75.

3. For early history see E.P. 1717, 1868; 827, 1875. A. E. Healey (E.P. 185, 1878) treated paper with "copperized ammonia."

4. F.P. 203741, 1890; see J. Persoz, *Rev. gen. mat. col.*, 1899, No. 27, 86; C. Suvern, "Artificial Silk," 1900, 78.

5. Inasmuch as the patent of Depeissis, although canceled in 1892 on account of non-payment of the renewal fees, remains as a document, the legal value of the Pauly patents is a debatable question.

6. D.R.P. 98642, 1897; E.P. 28631, 1897; F.P. 272718, 1897.

viously described process of Depeissis.<sup>1</sup> Two years later<sup>2</sup> M. Fremery and J. Urban took out their first patent embodying the details of the process, which, in conjunction with the researches of E. Bronnert,<sup>3</sup> led to the founding of the Vereinigte Glanzstoff-Fabriken at Elberfeld, Germany, which has been very successful commercially in the development of the art<sup>4</sup>. The work of R. Linkmeyer in this field begins in 1904,<sup>5</sup> and has been prolific in overcoming difficulties inherent in the various phases of the process. A. Bloxam in England has patented notable advances for the Glanzstoff Company,<sup>6</sup> while J. Bemberg,<sup>7</sup>

1. The English Specification has since been restricted by an amendment, so that the original claim of Depeissis, of the addition of a portion of some albuminoid substance to the solution, has been omitted in the latter specification.

2. E.P. 6557, 6641, 6656, 6735, 18884, 20630, 24101, 1899; 4303, 1900; U.S.P. 617009, 1899; 650715, 661214, 1900; 691257, 705748, 1902; F.P. 286692, 1899, and First Addition thereto, dated Oct. 14, 1899; 286726, 1899, and First Addition thereto, dated Dec. 4, 1899; 286925, 1899; D.R.P. 111313, 1899.

3. Bronnert, E.P. 18260, 18884, 1899; 4303, 1900; U.S.P. 646351, 646381, 646799, 1900; Bull. Muhl., 1900, 177; Mon. Text. Ind., 1901, 16, 817.; Bronnert and Fremery, E.P. 22092, 1907; Fremery, Bronnert and Urban, U.S.P. 658632, 1900; 672350, 1901; 698254, 1902; 856857, 1907; E.P. 20801, 1900; Fremery and Bronnert, U.S.P. 804191, 1905; Fremery and Urban, U.S.P. 650715, 1900; 705748, 1902; abst. J.S.C.I., 1897, 16, 355; 1900, 19, 239, 240, 344, 531, 659, 819, 821, 1105; 1901, 20, 38, 119, 1207, 1231; 1902, 21, 1150; 1905, 24, 1251; Ind. Text., 1900, 16, 352.

4. This company, with headquarters at Elberfeld, are said to employ at present over 7,000 hands, other works being at Niedermorschweiler, managed by Bronnert, and Oberbruch, Germany, managed by Fremery and Urban, and are also interested in works at Givet and at Izieux, France. "Givet Silk" was so named from this firm's product manufactured at Givet. The Spanish branch, the Sociedad Española de seda Parisien, has ceased operations. The British Glanzstoff, Ltd., has started works at Flint, of a capacity to ultimately employ 2,000 hands.

5. U.S.P. 795526, 1905; 839013, 839014, 1906; 842568, 852126, 857640, 866371, 1907; E.P. 1501, 4746, 4755, 4761, 4765, 6356, 1905; 3549, 3566, 16088, 1906; F.P. 346722, 347960, 1904; 350889, 352528, 353187, 356402, 357837, 361061, 1905; D.R.P. 183557, 185139, 1904; abst. J.S.C.I., 1905, 24, 238, 438, 670, 671, 888, 967, 1011; 1906, 25, 120, 371, 473, 1090; 1907, 26, 197, 252, 406, 606, 868, 1088.

6. E.P. 1283, 1284, 1745, 1905; F.P. 351206, 351207, 351208, 1905; abst. J.S.C.I., 1905, 24, 855, 856. See Vereinigte Glanzstoff-Fabriken, D.R.P. 218490, 1907.

7. D.R.P. 162866, 1900, and First Addition thereto, D.R.P. 174508, 1905, in which it is claimed that a copper hydroxide cellulose, readily soluble in ammonia, is obtained by the action of alkalis on a mixture of cellulose and copper; for example, a mixture of cotton and copper is wetted with water (100-150% of the weight of the cotton) and ammonia is either added as a solution or the gas is passed over the mixture. The resulting blue mixture is said to be readily soluble in ammonia, giving highly concentrated cupro-cellulose solutions. Lecoecur (F.P. 381939, 1906; 392868, 392869, 1908; E.P. 14143, 28149, 1908; U.S.P. 967397, 1910; abst. J.S.C.I., 1908, 27, 221) dissolves cellulose in an ammoniacal cupric hydroxide solution and forces through a capillary orifice into a coagulating bath in the usual manner, but the bath is maintained at a temperature of 27-35°, and consists of a mixture of equal parts of a solution containing 44-49% NaOH and a solution containing 23-28% anhydrous sodium carbonate. A rather weaker bath is employed for artificial hair. After spinning the thread is wound on a bobbin, and plunged into a second coagulating bath containing in solution the same amount of carbonate as in the first bath, but only about 7-8% NaOH. The copper and ammonia are eliminated by a passage through a dilute solution of ... to which 1-4% free acid has been added. The original solution is forced through the orifices at a pressure between 1 and

E. Berenguer,<sup>1</sup> C. Bouequy,<sup>2</sup> J. Chaubet,<sup>3</sup> L. Cuntz,<sup>4</sup> E. Eck,<sup>5</sup> J. Foltzer,<sup>6</sup> A. Kracht,<sup>7</sup> W. Lake,<sup>8</sup> A. Lecocur,<sup>9</sup>

1.5 k. where size denier 30, 25, and 20 (i.e., 450 meters per gm.) is desired. Especial emphasis is placed upon the necessity of a thorough treatment of the thread in the second bath, where it should remain for at least a half hour.

1. E.P. 10545, 1907, in which the solutions in concentrated form are prepared by treating moist cellulose with an ammoniacal solution to which is subsequently added cupric carbonate.

2. F.P. 376065, 1907, the prescribed formula being cellulose (14 parts) immersed in a mixture consisting of ammonia (100), water (100), sodium hydroxide (10 parts) and copper acetate. The cellulose fibers thus become swollen, and a further addition of sodium hydroxide (5 parts), water (10) and ammonia (10 parts), is said to bring the cellulose completely into solution.

3. E.P. 14525, 1899; see L. Collardon, U.S.P. 953319, 1910.

4. In the manufacture of artificial silk from cuprammonium solutions of cellulose, specially favorable results as regards luster and strength are said to be obtained by the use of a coagulating bath consisting of a very concentrated solution of sodium hydroxide. According to the author's invention (F.P. 383412, 383413, 1907), results equally satisfactory are afforded by a coagulating bath containing only a small proportion of alkali hydroxide together with a large proportion of a chloride of an alkali or alkaline-earth metal. Suitable baths are prepared by dissolving 30 parts of sodium or calcium chloride and 3 parts of sodium hydroxide in 100 parts of water.

5. E. Eck and E. Bechtel, U.S.P. 839825, 840611, 1907.

6. F.P. 345687, 1904; 369402, 1906, in which the cellulose, dissolved in cuprammonium solution or other solvent, is led from a reservoir on to a revolving surface, while one or more felting machines blow animal or vegetable fibers on as it leaves the orifice. The cylinder revolves in a bath of coagulating liquid such as sulphuric acid, etc. The coagulum is detached from the revolving surface by a knife, and, after being pressed between two cylinders, enters a second bath containing concentrated caustic soda or potash solution, where complete precipitation under tension takes place. The excess of liquor is then removed, and the material is at the same time stamped with the desired design, and finally washed in dilute acid.

7. F.P. 355064, 1905, the method consisting in forcing a concentrated solution of cellulose in ammoniacal cupric oxide solution, 5 to 10%, through a hole larger than the size of the desired thread, treating the product in a sodium carbonate bath, then drawing the threads out to the desired fineness, and, when hardened, introducing them into a 35% solution of caustic potash or soda.

8. E.P. 3549, 1906; according to Soc. Anon. pour l'Etude Ind. de la Soie Serret (F.P. 363949, 1906), water-resisting artificial silk having the same tenacity in the wet as in the dry state, is produced by coating natural silk fibers with cellulose by passing them through a solution of the latter. To protect them against the action of the solvents employed, the silk fibers may be treated with formaldehyde or other compounds having a similar action upon them. The fibers thus coated are spun either together with one another, or with uncoated silk fibers. In the latter case, the uncoated fibers are preferably stretched while being spun or twisted with the coated fibers, so that when the yarns produced are submitted to tension, the strain may be chiefly borne by the uncoated fibers.

9. E.P. 16442, 1906; 14143, 28149, 1908; F.P. 374277, 381939, 1906; according to this investigator in the precipitation of cellulose from its solution in cuprammonium, the use of acids in the coagulating liquid tends to give products which are milky or opaque and not over strong. With alkalis the threads obtained are clear, supple and strong, but though suitable for the manufacture of thick threads, such baths cannot be used for the preparation of threads of a fine or even medium titer. The best results are obtained by using solutions of the bisulphates of the alkali metals, of such strength that coagulation is instantaneous and the ammonia and copper hydroxide completely neutralized. Upon leaving this first bath the threads traverse a second, more dilute one, and are finally obtained in a supple, elastic and strong condition. Solutions of colloidal hydrated cuprammonium oxide can be prepared in two ways: firstly, by treating a solution of a copper salt with ammonia and caustic alkalis with subsequent dialysis of the solution, and

R. Müller,<sup>1</sup> R. Pawlikowski,<sup>2</sup> J. Vermeesch,<sup>3</sup> and others<sup>4</sup> have contributed

secondly, by the simultaneous action of air and ammonia on metallic copper with subsequent dialysis. The liquors thus prepared will be hereafter referred to as liquors *A* and *B* respectively. If liquor *A* is so prepared as to contain more than 12 gm. of copper per l., it contains deleterious compounds which cannot be removed by dialysis. A solution containing only 12 gm. of copper per l. is, however, only capable of dissolving a small amount of cellulose, and this proportion is too small for the manufacture of a strong filament. It is found that the best product is obtained if a mixture of the two liquors be employed, the proportions being such that the resulting mixture contains about 25 gm. or more per l. of copper in the state of colloidal hydrated cuprammonium oxide, but of which no more than about 12 gm. of copper per l. is derived from liquor *A*.

1. U.S.P. 779175, 792888, 1905. F. and A. van Bosch, and O. Müller (E.P. 6942, 1906) have found that cellulose articles, such as threads, films, etc., prepared by dissolving the cellulose of cotton-seed hulls by the ordinary solvents of cellulose (E.P. 3211, 1906) may be produced in a range of colors varying from red to pale yellow, by leaving in the cellulose a certain proportion of the natural coloring matter of the hulls. Darker shades can be obtained by adding to the cellulose the desired proportion of the colored alkaline liquor obtained in the first stage of the treatment of the cotton-seed hulls. The colored solutions of cellulose are formed into solid articles by precipitation in solutions with an acid reaction.

2. In this process (F.P. 403488, 1909) cellulose is steeped for several hours in a solution of copper oxychloride in aqueous ammonia, until it is practically all dissolved. Copper oxychloride is a substance of variable composition, but about 90 gm. of it and 850–900 cc. of ammonia of sp.gr. 0.93 will generally suffice for dissolving 100 gm. of cotton wool. The cupric oxychloride may be employed in admixture with other compounds of copper, such as cuprous oxychloride, cuprous chloride, cuprous oxide, cupric oxide, cupric carbonate, or cupric hydroxide. It is stated that the solution of the cellulose takes place more rapidly and completely than with the ordinary cuprammonium solutions, owing to the presence of the chlorides, and it is not necessary to subject the cellulose to a preliminary treatment with alkali hydroxides or powerful bleaching agents. The cellulose is precipitated from the solution by treatment with dilute acids.

3. U.S.P. 836620, 1906; E.P. 9251, 1906; E.P. 365057, 1906; in which is described a process of manufacturing glossy textile fibers from a solution of cellulose in copper ammonia, discharged in the shape of fine jets from capillary orifices, consisting in introducing the jets into a precipitating liquid consisting of acidulated or alkalinized glycerol, or monosulphoglyceric acid in water and glycerol, the threads being subsequently introduced into a neutralizing bath consisting of a soluble salt, as NaCl, in which sulphuric acid can be substituted for the constituent acid, employing a dilute solution of sodium bisulphate followed preferably by washing. See also Vermeesch, U.S.P. 850695, 1907.

4. Meister, Lucius and Brining (U.S.P. 779175, 1905; E.P. 21988, 1904; E.P. 350220, 1905; abst. J.S.C.I., 1905, 24, 129), introduce cuprammoniacal solution containing about 5% of hydrated cellulose into a caustic soda solution of about 40%, then treats with sulphuric acid of 12%. The Hanauer Kunstseidefabrik, Hanau (E.P. 10164, 10165, 1907) pass cellulose, dissolved in an ammoniacal solution of cupric oxide, from an opening or former, through heated caustic soda solution so as to form a film inclosing a liquid internal portion, then exposing the product to the air until it becomes solidified throughout, and then passing it through caustic soda solution and if it be desired to decolorize the product subjecting it to the action of acidulated water. They find (D.R.P. 220711, 1907; 222893, 1908) where sulphites are used as coagulants, more brilliant fibers are produced, whereas bisulphites favor a more thorough coagulation and production of thinner fibers. The washing out of the copper, which for the greater part goes into aqueous solution as copper tetra-aminesulphite, is readily effected. In their D.R.P. 221041, 1908, cuprammonium cellulose solutions are forced through fine orifices into coagulating bath consisting of cold or warm, saturated solutions of bisulphites, e.g., sodium bisulphite. The coagulating bath may be reinforced, during the process, by passing sulphur dioxide through it. The fibers are then



mainly along the lines of preparing ammoniacal solutions in which the minimum of ammonia is used and in the mechanical details of spinning acceptable filaments. Many of the suggestions herein recorded and changes advocated are too recent for time to have demonstrated their respective merits. The different precipitating solutions, preliminary treatment of the cotton or cellulose, solution of the copper from the spun filament, alkali solvent recovery and production of maximum luster, are the topics which apparently have received the most minute attention.

The process in general requires very great care and attention to detail for commercial success, a condition of uniform low temperature, and a fixed ratio between copper, ammonia and cellulose.<sup>1</sup> The latter gives best results when mercerized or oxidized, the finished thread, in its dyeing properties at least, deporting itself like an oxycellulose.<sup>2</sup> Cuprammonium filaments are no more inflammable than cotton cellulose. A former great drawback to the success of this process lay in the fact that cellulose cannot readily be dissolved directly in large quantities of ammoniacal oxide of copper in such a manner that the solution may present a degree of concentration sufficient to permit

washed with dilute acids to remove the traces of copper, then washed with water and finally treated with sodium carbonate solution at a temperature about 70°. The ammonia is readily recovered from the coagulating bath after the process, while the copper, which is chiefly present in its tetramine sulphite, can be easily removed from the fibers by washing. See also Consortium Mülhousien pour la Fabrication de Fils Brillants (E.P. 13331, 1899); H. Reisenfeld and F. Taurke, Ber., 1905, 38, 2798. G. Guadagni (E.P. 1265, 1908; 25986, 1910; F.P. 386339, 1908; D.R.P. 216669, 1908; abst. J.S.C.I., 1908, 27, 682) has devised an apparatus for producing copper-ammonia-cellulose solutions with a view of effecting a more ready action at a lower temperature, whereby the Schweitzer solution is overlaid with the moist cellulose and through the solution air is blown and then, saturated with ammonia, is led through the moist cellulose, thereby effecting the solution of the latter.

1. E. Berl (Chem. Zeit., 1910, 34, 532) has investigated the formation and properties of cuprammonium-cellulose, and finds that only ammoniacal solutions of copper hydroxide or of basic copper salts dissolve cellulose; ammoniacal solutions of crystalloid copper-tetramine sulphate,  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ , do not dissolve it. The viscosity of cuprammonium-cellulose depends on the previous preparation of the cellulose, the quantity dissolved, and the age of the solution. The solution greedily absorbs oxygen, oxycellulose of little value for spinning, being formed. On dialyzing cuprammonium-cellulose in ammonia, a jelly is obtained, which on drying *in vacuo* over sulphuric acid, gives a blue powder, soluble in ammonia, and containing 69.5% of cellulose and 30.5% of copper hydroxide. A greenish-blue powder soluble in ammonia and containing 62% of cellulose is obtained by precipitating cuprammonium-cellulose with formaldehyde. Alcohol precipitates a mixture of cellulose and black cupric oxide, which is no longer soluble in ammonia. The formation of cuprammonium-cellulose is stated to be a colloidal phenomenon, the colloidal portion of the cuprammonium hydroxide joining the cellulose to form an adsorption product soluble in ammonia; this explains the various reactions and the want of stoichiometric ratios between the copper and cellulose on solution and precipitation.

2. Prud'homme (Jour. Soc. Dyers, 1891, 148); E. Bronnert (Rev. Mat. Col., Sept., 1900, 267), notes that the hydrocellulose of Girard is almost insoluble in cuprammonium, as is starch, but is rendered soluble by alkali treatment.

of spinning acceptable filaments. Of the numerous processes suggested to overcome this obstacle, nearly all have been based upon the energetic action of fixed alkalis before the solution, with a view to producing a previous dehydration of the cellulose.

Cuprammonium silks, as compared with those prepared from the cellulose nitrates, are not combustible or explosive, are equal to the latter in tenacity and elasticity, and do not possess the seroop (rustle) of natural weighted silk. The methods of production are free from danger, no inflammable solids or solvents being employed, and the denitration process (so expensive and troublesome in the Chardonnet silks) has no counterpart in cuprammonium filaments. The relative point of expense is a debatable question. While at first glance it might seem that the absence of the denitration process would place the cuprammonium silks at a much greater advantage as to cost of production, the advocates of the nitrocellulose silks have called attention to the multitude of mechanical refinements in production as a tendency to offset this. When these filaments are placed in water they often display an easily observed fluorescence which the nitro silks do not.

**Glanzstoff Silk or Givet Silk**, also known as "Parisian Artificial Silk," "Soie de Paris," "Lustra Cellulose," "Oberbruch Silk," and "Artiseta," is the development of Fremery, Urban and Bronnert, and is, commercially, the most successful of the cuprammonium-cellulose processes. While Depeissis proposed to prepare the cellulose solution by dissolving cellulose at the ordinary temperature in the ammoniacal copper solution, the mode of working was defective because the liquid was too slow in dissolving the cellulose, often two weeks being required, and furthermore, the solutions were so dilute that the percentage of contained cellulose was relatively small. Moreover, solution was always accompanied by oxidation, which greatly changed the cellulose molecule, and in a manner detrimental to the spun filament. In the II. Pauly patent<sup>1</sup> this oxidation is materially reduced by preparing

1. H. Pauly, E.P. 28631, 1897; F.P. 272718, 1897; D.R.P. 98642, 1897; Sw.P. 16077 (issued to Fremery and Urban). It is claimed that Fremery and Urban took out these patents under the name of Pauly. The original process consisted in freeing cellulose from fats and oils by dilute caustic soda, then dissolving in ammoniacal copper solution prepared by dissolving copper turnings (preferably mixed with the turnings of a more electro-magnetic metal such as platinum) in an upright tube, allowing the aqua ammonia to trickle down, and at the same time forcing oxygen up the column. The best strength of solution was found to be 15 gm. copper per liter in which about 45 gm. of cellulose would dissolve by digesting for about eight days. To prevent the cellulose precipitating and decomposing, the temperature was kept below 30°, the solution filtered through glass wool or sand by suction, coagulated by dilute acetic acid, and dried in warm air. Lengthy descriptions of the Pauly process to be found in the literature, are descriptions of the subsequent refinements of Fremery, Bronnert and Urban.

the solution in the cold, after the method originated by J. Mercer. Still solution of the cellulose was slow. Bronnert materially reduced the length of time necessary to properly effect this solution, by first transforming the cellulose into its hydrate.<sup>1</sup> The soda cellulose formed is then triturated with finely divided crystallized copper sulphate, and subsequently treated with ammonia, the substances being used in the proportion of their combining weights as follows: 162 parts by weight of air-dry cellulose (cotton or purified wood pulp) in a finely comminuted state, 80 parts NaOH and 500 parts water are brought together, stirred thoroughly and after the lapse of an hour or two, 250-255 parts (theory calls for 249) blue vitriol crystals are added in small quantities in order to keep down the temperature, a pale blue, uniform mass resulting. Aqua ammonia of 26° Bé. is then poured over in amount equivalent to about 15 molecules. Solution readily takes place, a semitransparent and viscid mass resulting. When the sodium sulphate formed as the result of the interaction subsides, the supernatant solution is separated by decantation.<sup>2</sup> The reaction is considered finished and the fluid suitable for spinning when 4-5 cc. run from a burette or other small orifice forms a continuous thread.<sup>3</sup>

1. W. Normann (G. Z. Celluloid Suppl., 1906, **21**, 3; from Chem. Ztg., 1906, **47**) finds that cellulose impregnated with a solution of copper hydroxide in caustic soda produces a copper soda cellulose compound containing 1 molecule cupric oxide for 2 molecules cellulose, that this compound is insoluble in dilute ammonia, and that this is the reason why a solution of cellulose in Schweitzer's reagent can be precipitated by sodium hydroxide solution, as in the manufacture of artificial silk. In E.P. 20801, 1900, Bronnert, Fremery and Urban, the cellulose is dissolved in a concentrated "solution" of cupric carbonate in a 16-18% solution of ammonia. In Bronnert's preferred formula, 100 k. cellulose are mixed with 1,000 l. of a solution containing 30 k. sodium carbonate and 50 k. caustic soda, and warmed in a closed vessel for about 3½ hours under a pressure of 2½ atmospheres, the mercerized cotton thus obtained being dried, bleached, washed, and again dried, when it is ready for the cuprammoniacal solution (Schweitzer's reagent). The Rheinische Kunstseide Fabrik Akt.-Ges. (F.P. 405571, 1909) describe a process in which cottonseed hulls is utilized as the source of cellulose. The solvent is prepared by treating 1-3 parts of solid copper sulphate with 2-4 parts of a solution of sodium hydroxide at 21° Bé. and adding to the mixture 5-15 parts of aqueous ammonia of 25° Bé. The solution is then cooled to 0°, the crystals which form are separated, the liquid being sufficient for dissolving one part of cellulose at any convenient temperature.

2. U.S.P. 658632, 1900; 672350, 1901; the temperature of solution being kept within -5° to +5°. See also Fremery and Urban, E.P. 6641, 21101, 1899.

3. U.S.P. 646351, 661214, 1900; the cuprammonium is prepared by forming a saturated aqueous solution of cupric sulphate, filtering on account of the separation (among other things) of a small amount of cupric carbonate from the carbonates normally present in the water, or by the addition of a small amount of sulphuric acid, which, by dissolving the copper carbonate, causes the solution to clear up again. Ammonia is then added in small portions and with much agitation of the copper solution, a pale blue precipitate of cupric hydroxide being formed. Addition of ammonia is continued until a drop of the filtrate produces no precipitate with ammonia, but does precipitate blue upon addition of a drop of a cupric salt. The mixture is then brought into a centrifuge containing a felt lining, the ammonium sulphate formed in the reaction removed and used for fertilizing purposes, and the cupric hydroxide washed practically free from sulphates. Ammonia is then again added, when the copper passes into the deep blue solution

without visible solid<sup>1</sup> particles.<sup>2</sup> It is then forced under a pressure of 1.5–2 atmospheres through a draw plate containing holes 0.12–0.15 mm. in diameter, into a precipitating bath of acid or alkaline glycerol, sodium chloride or sodium bisulphate, to remove the copper present in the filaments.<sup>3</sup>

The washing is an important division of the process, for in contradistinction to the ordinary porous and absorbent cotton thread, the gelatinous and difficultly permeable cuprammonium filament is not readily penetrated by fluids. In the preferred method of washing of Fremery and Urban<sup>4</sup> in which the threads are spooled or in a coiled-up condition, they are brought in contact only with comparatively small quantities of the washing fluid in order not to dilute too suddenly the liquid adhering to or contained in the threads, and thereby avoid the formation of insoluble basic salts, or combinations with the salts used in dissolving the cellulose. This may be best effected, according to the patentees, by causing the water to flow

of cuprammonium, a small amount of ferric hydroxide (from iron always present in commercial blue vitriol), being removed by filtration. Although an excess of ammonia in the solution is not detrimental, it is a useless expenditure of money. A satisfactory working concentration of the cuprammonium is such that each liter of solution contains between 10–15 gm. copper, solutions of this copper content being capable of dissolving 45–50 gm. cotton cellulose. Hime and Noad (E.P. 7716, 1889) facilitate the oxidation of the copper electrolytically; C. Wright crumples up sheet copper, places in a tall cylinder and covers with ammonia, when atmospheric air is caused to bubble through the liquid column at a speed equivalent to about 40 times the volume of liquid used per hour, the process requiring about six hours. Erdmann (J. pr. Chem., 76, 385) concludes that the cuprammonia solutions of cellulose are not, strictly speaking, solutions of cellulose at all, the latter being rather diffused and gelatinized through a highly hydrated and attenuated solid. On the other hand, Cramer has apparently demonstrated by osmotic pressure experiments that this inference is untenable, and that the solution of the cellulose may be more properly considered as complete.

1. U.S.P. 804191, 1905; E.P. 1283, 1284, 1905; F.P. 351206, 351208, 1905; D.R.P. 169567, 1905. Inasmuch as the solubility of the cellulose decreases as the temperature of the cuprammonium salt solution increases, while the decomposition of the cellulose increases with increasing temperatures, the mixture should be kept comparatively cool until the cellulose has been completely dissolved in order to prevent decomposition.

2. In E.P. 22092, 1907, the patentees claim that when the cellulose is precipitated from its cuprammonium solution by passing into a solution of caustic soda at a temperature of 45°–60° the decomposition of the cellulose solution is almost instantaneous, and the speed of drawing off the thread may be increased over that employed when the caustic soda solutions are used at a lower temperature, without fear of breakage. The products obtained at 45°–65° take up dyestuffs more strongly than those obtained at 40°.

3. In E.P. 9268, 1907, saccharose and lactose are claimed as precipitating liquids, at a temperature of 45°–75°, when the process used is that described in E.P. 27707, 1907.

4. U.S.P. 661214, 1900; 705748, 1902; the reason given for washing successively with small amounts of water is that by bringing cellulose filaments in contact with a great bulk of water, basic salts such as zinc oxychloride, or insoluble metallic compounds such as cupric hydroxide readily form, and which cannot be eliminated by continued washing with water alone. For utilizing the refuse from the manufacture of artificial silk from cellulose see Verein. Glanzstoff-Fabr., E. P. 15700, 1910.

successively over a number of spools of filaments, and arranged one over the other. The supply of washing liquid is so regulated as to bring only such small quantities (and this is important) at once into contact with the spooled cellulose, when the formation of insoluble basic salts is prevented. As soon as the uppermost spools are entirely washed they are removed, the lower spools being successively transferred from below upward, and nearer to the supply of wash water.

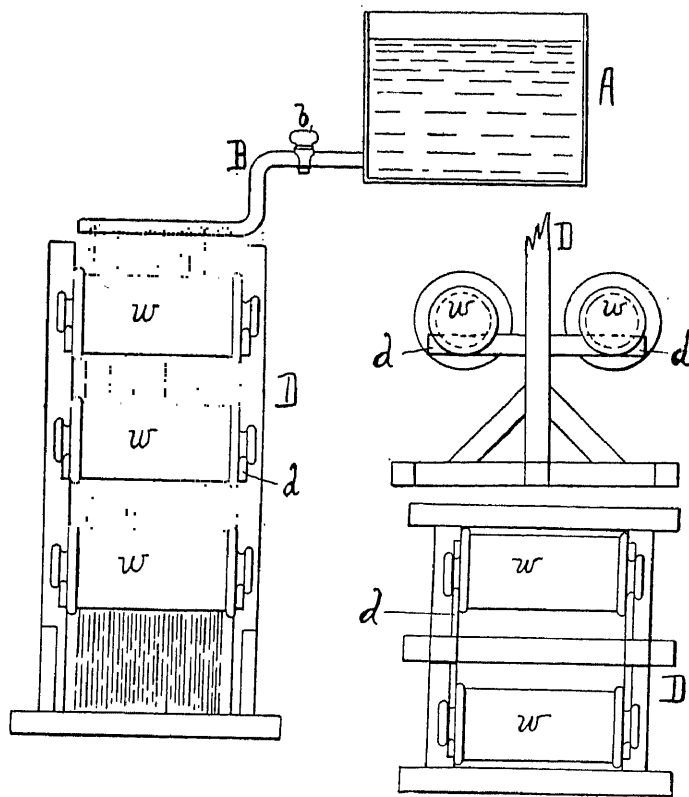


FIG. 137.—Washing Artificial Filaments According to Fremery and Urban.

This method of washing is shown in Fig. 137, in which *A* denotes a suitable reservoir or other source of supply for the washing liquid with one or more delivery pipes *B*, having cocks or valves *b* and perforations in those portions of the discharge-pipes which lie immediately over the superposed spools *w* of cellulose threads to be washed. These spools *w* are mounted on arms *d*, arranged in a suitable frame *D*, so that they can be readily transferred from one pair of supporting-arms to another.

In a more recent<sup>1</sup> invention these inventors claim that when an ammoniacal cupriferous solution of cellulose prepared at a temperature below 10°, as described in U.S.P., 617009, is projected through a suitable opening, such as a slit or a comparatively wide cylindrical orifice into a strong caustic alkali solution, that is to say, a solution having a sp.gr. of 1.280–1.320, the film produced in one case and the thick thread in the other are brilliant, strong and elastic, and are, moreover, waterproof even when they have been washed with acid to remove the copper they contain. Thus the thick threads made in one operation, that is to say, without spinning several fine threads together, as has been customary heretofore, are excellently suited as substitutes for horsehair.

The following examples illustrate the invention:

Two hundred and forty k. of cellulose, previously treated successively with a cold concentrated solution of caustic soda and an oxidizing bleaching agent is described in U.S.P. 646531, are dissolved in, say, 3,000 l. of a cupriferous ammoniacal solution at a low temperature in the usual manner, and the solution is injected through capillary tubes into a strong solution of caustic soda, preferably a cold solution containing not less than 20%. The threads of coagulated cupriferous cellulose thus produced are wound up, washed with water until free from adhering caustic soda, and dried under tension.<sup>2</sup>

Another modification of the process results from<sup>3</sup> projecting cellulose in a cupric ferrous ammoniacal solution, through capillary tubes into a liquid capable of precipitating the cellulose, such as dilute acetic acid, winding the wet thread thus produced onto a roller revolving in a bath of dilute acid, such as acetic, and after washing away the copper and ammonia drying under tension. The economical value of the process resides in the fact that both the ammonia and copper can be recovered from the acid solution. When, however, the process is used for making threads of considerable thickness or for making films, to which purpose large capillary tubes or slit-shape openings must be used for the injecting apparatus, the threads obtained

1. See U.S.P. 856857, 1907; E.P. 16495, 1907.

2. U.S.P. 804191, 1905; in E.P. 16495, 1906, the threads or fibers passing from the nozzles through the precipitating liquor are laid in groups on conveying bands which move in an upward direction, at a speed regulated to the rate of flow from the nozzles. On these bands the fibers are washed or irrigated (on the counter-current principle, so that the chemicals used can be easily recovered) to free them from the precipitating liquid, and then passed to cylinders upon which they are dried.

3. E.P. 1283, 1905; see E. Brandenberger, E.P. 15190, 1909; J. Brandenberger, E.P. 24809, 1908; F.P. 405429, 1908; abst. J.S.C.I., 1909, 28, 851.

are so dull and inelastic that they are practically useless, and the films are not transparent, being brittle and tender.

To produce thick threads, films and ribbons<sup>1</sup> cuprammoniacal cellulose solutions are injected through slits, into strong caustic-alkali solution, and afterwards immersing the forms thus produced, before they are washed into a cold strong solution of caustic alkali; containing no less than 20% NaOH or treating them centrifugally with such solution for a shorter period. This solution may be that into which the cellulose solution was injected in order to produce the form, in which case it will contain a little ammonia; the ammonia is advantageous provided it does not exceed about 6% of the solution, when it begins to dissolve the surface of the cellulose form, and thus to roughen it.<sup>2</sup>

It is better, however, to use a fresh solution of caustic soda, and to apply it with aid of centrifugal action, such as that adopted in mercerizing hanks of cotton. For instance, the threads may be wound on the perforated drum of a high-speed centrifugal machine, and the caustic soda solution may be introduced through an axial perforated pipe; after some two minutes water is substituted for the caustic soda solution, and finally the threads are rinsed in acid and dried under tension. Or the skeins, impregnated with caustic soda, are introduced into the centrifugal drum and sprinkled for some minutes with caustic soda solution while the apparatus is in operation, then with water, then, if necessary, with acid, and afterwards with water; drying under tension follows.

In this manner the cellulose form, it is said, becomes more transparent, clear, stronger, and more elastic. These enhanced properties are retained if, after the alkali treatment, the form is treated by acid or another suitable solvent to extract the whole or a part of its copper.

The duration of the treatment with the alkali is determined by the thickness of the form, as the thicker it is, the longer it resists penetration by the alkali.

1. E.P. 1745, 1905.

2. E.P. 6557, 1899, prepares the cellulose for solution by treating for twelve to eighteen hours in a bleaching bath corresponding to 15 gm. "chloride of lime" per l.; E.P. 6735, 1899, dries the formed filament below 40° in a vacuum; while E.P. 20630, 1899, describes a method of removing water from the threads by first dipping the threads or films into hot water or steam to render them porous, and then drying as in previously mentioned process. This method of drying after immersion in hot water or steam is based upon the observation that the drying process takes place in two distinct steps, the first being upon the removal of the mechanically held moisture, and takes place comparatively rapidly. The second step in evaporation takes place very slowly, explainable on the supposition that this moisture is chemically combined with the cellulose. The object of submerging partially dried cellulose in hot water is to break up the loose chemical union between water and cellulose, the process of drying, it is claimed, being then effected in one-quarter of the time which would otherwise be required.

The process is claimed to be particularly applicable for making thick, highly elastic, transparent, and unusually strong threads and films, such as artificial horsehair, embroidery threads, and photographic films. The threads, after carbonization, serve as electric-light filaments, and the carbonized films for telephonic purposes. To avoid deformation, the forms made according to this invention must be dried under tension, but preferably at the ordinary temperature. The decomposition of the cuprammonium by the dilute acid used as the coagulating medium for the formed filaments, changes the copper into a salt, usually the sulphate. Ammonium sulphate is also present, the method of recovery of the copper depending on the disposition to be made of the ammonia. Perhaps the simplest way is to deposit the copper upon loose thin sheets of iron laid in the solution, an amount of iron being dissolved corresponding to the quantity of copper precipitated. The separated copper requires but careful washing, to be reused after solution in sulphuric acid, or the fine copper may be directly dissolved in ammonia. To recover both ammonium sulphate and copper, the liquid is neutralized with ammonia, thus forming ammonium and copper sulphates. By addition now of more ammonia, cupric hydroxide separates and all the copper may thus be precipitated and immediately used. The solution of ammonium sulphate is most economically utilized direct as a fertilizer, being too dilute to evaporate to dryness and recover the solid salt.

**R. Linkmeyer** has solved many of the problems connected with the production of cuprammonium cellulose filaments, his method being to first immerse the cellulose in a weak bath of ammoniacal cupric oxide in order to induce superficial swelling of the cotton fibers and the deposition of metallic copper thereon,<sup>1</sup> the active solution being effected in a subsequent and concentrated solution of copper in ammonia. In this manner is obtained sufficient cellulose dissolved in a unit volume of fluid to give the viscosity advantageous for spinning.<sup>2</sup> The process may be applied commercially as follows: Seven gm. cotton, freed from grease and bleached, are placed in 150–180 cc. of ammoniacal copper oxide solution containing about 12 gm. copper and 90 gm. ammonia per l. and to which there has previously been added, 6 cc. caustic soda solution of 40–50° Bé. After remaining

1. U.S.P. 795526, 1905; E.P. 4755, 4761, 1905; F.P. 346722, 1904; 353187, 356402, 1905.

2. The first bath serves to soften, swell and disintegrate to some extent the fibers and to fix upon them the oxide of copper dissolved by the ammonia. The fibers then dissolve speedily and readily in a concentrated solution of ammoniacal copper oxide. By proceeding in this manner it is claimed the conversion of the cellulose into oxycellulose or the hydration of the fibers is avoided. Further, the success of the solution depends less upon the temperature than upon the other processes. Solution takes place as well at 10–15° as at a lower temperature.



for 2-3 hours in this bath, the fibrous material is removed and freed from excess of liquid by pressure and then dissolved in 100 gm. ammoniacal cupric oxide containing 16-18 gm. copper and 200 gm. ammonia per l. In this manner a viscous solution is obtained which may be diluted with water, and after careful filtration is ready for conversion into filaments. In order to decrease the fragility of threads spun into a dilute sulphuric acid coagulating medium Linkmeyer has observed<sup>1</sup> that the weakening of the filament appears to be due to the fact that a large part of the ammonia becomes free in the solution after the cellulose has been dissolved. In order to overcome this weakening tendency a portion of the ammonia in the cellulose solution is removed by a vacuum before the filaments are formed. By this previous extraction of uncombined ammonia, dilute sulphuric or other mineral acid may be used as the coagulant and copper solvent without seriously affecting the tensile strength of the finished filament. In order to increase the brilliancy of the threads, the following method of operating is advocated:<sup>2</sup> the solution from which the free ammonia

1. U.S.P. 839013, 839014, 1906; E.P. 4746, 4765, 6356, 1905; 3549, 1906; F.P. 347960, 1904; 352528, 357837, 361061, 1905; D.R.P. 183557, 1904.

2. Linkmeyer and M. Pollak, U.S.P. 842568, 1906; E.P. 1501, 1905; F.P. 350888, 1905. Whatever liquid is employed for the precipitation, the thread obtained generally lacks strength, especially in the moist condition. This remark is particularly applicable to threads obtained by precipitation in acetic acid or in a relatively concentrated acid of from 30-65%. The reason for this want of strength would appear to be due to a sort of decomposition produced by the presence of free ammonia in the solutions before the precipitation or in the coagulated threads at the moment at which they are to be submitted to the acid washing. When fixed alkalis are employed for effecting the precipitation, the threads obtained present an opaque appearance, which is apparently likewise attributable to the effects of this decomposition, and it is probably owing to this opacity that the employment of alkaline liquids for the precipitation has not become general, because it had already been noticed that they produced stronger threads. This peculiarity has been utilized in the manufacture of a kind of felt, E.P. 3161, 1899.

If soda or potash lyes are employed for the precipitation bath Linkmeyer claims merely a coagulation is produced, part of the ammonia passing into the precipitation bath, and after the washing of the threads with acid it is found that they are stronger than those precipitated in acids. If, however, immediately after leaving the precipitation bath the ammonia still contained in the threads is eliminated as completely as possible before freeing them from the oxide of copper that they still contain by a washing with dilute acid, their strength will be largely increased and the decomposition referred to above will not take place.

The elimination of the copper by washing is effected particularly readily when the oxide of copper has been converted into a salt dissolving readily in acids for example, into copper carbonate.

In order to eliminate the ammonia from the freshly formed threads, they may be treated by means of air, which produces the evaporation of the ammonia and precipitates the copper as hydroxide, a portion of which is then converted into carbonate by the carbonic acid in the air. For example, the threads are wound upon a cylinder arranged outside the precipitation bath, which may be perforated and arranged in such a manner as to permit an injection or suction of air through the layers of thread. When the threads have been precipitated in a soda lye, for example, they leave it with a blue and transparent appearance, and by means of the treatment described above they gradually assume a pale blue tint and become opaque, and when their appearance no longer undergoes modification

has been withdrawn as described above; is caused to pass through small apertures into acid diluted to such a degree that it is not capable of instantly combining with the salts in the cupric solution, for example, sulphuric acid of 2-15% strength. Then the threads obtained are passed directly into caustic soda solution of 25-35° B<sub>é</sub>. strength. After rinsing in water to free from caustic, the threads are run into an excess of 5% sulphuric acid, agitated therein until neutral, rinsed and dried. If the threads are stretched to the extent of 1/5-1/25 of their length during the drying process<sup>1</sup> the brilliancy is also materially enhanced. If the stretching be done in the acid bath<sup>2</sup> the tension may be released during drying without the threads returning to their original length. In another differentiation<sup>3</sup> the threads are squirted into a gaseous atmosphere which is saturated with an atomized coagulant, by means of mechanical humidifiers, as of the Drosophor type. Linkmeyer has found<sup>4</sup> that it is possible to extract from an ammoniacal cupric-cellulose solution a large part of its ammonia without a precipitation of the dissolved cellulose taking place, this extraction being best effected by vacuum suction, and agitating the mass to facilitate liberation of ammonia gas.<sup>5</sup> In distinction from those processes in which the whole of the ammonia has been left in the solution of cellulose in order to subsequently precipitate it in the form of a salt corresponding to the acid employed, vacuum recovery permits of a considerable portion of the ammonia being regained in a form immediately available for reuse.<sup>6</sup> After the elimination of the uncom-

they are in the most favorable state for being submitted to washing with dilute acids, which imparts to them the transparency of glass and removes their coloration.

1. F.P. 350889, 1905. The process of H. Bernstein (U.S.P. 960791, 1910) apparently contains nothing new.

2. E.P. 16088, 1906.

3. D.R.P. 185139, 1904.

4. U.S.P. 842568, 852126, 1907; see also U.S.P. 945559, 1910; E.P. 4104, 1909; abst. J.S.C.I., 1909, 28, 934.

5. The exactness of the assumption that a portion of the ammonia is liberated as a result of the dissolution of the cellulose would appear to be demonstrated by the fact that if in a very complete vacuum a bath of ammoniacal oxide of copper is freed from all the ammonia not combined with the oxide of copper, cellulose then being dissolved therein, it is found, upon re-establishing the vacuum above the bath that large quantities of ammonia gas are again liberated.

6. In order to dissolve 1000 gm. cellulose from 3,000-4,000 gm. ammonia are required, and as the result of evaporation and other losses, there are used about 4,500 gm. ammonia per k. finished thread. It thus becomes evident that processes for ammonia recovery have a relatively high value. To still further reduce the cost of production, Linkmeyer (D.R.P. 206883, 1907; U.S.P. 962769, 1910; abst. J.S.C.I., 1909, 28, 362) replaces part or the whole of the alkali hydroxides used as the coagulating media by alkali or alkaline earth chlorides, it having been found that the latter can take the place of the more expensive former, when a small amount of sodium or potassium hydroxide is also added to increase the power of coagulation. In addition it has been observed that the structures coagulated in this manner have the same properties as those which have been coagulated in pure soda lye. In practice, about 28 k. sodium chloride are dissolved in 100 l. water, and 3-5 k. of sodium "oxidehydrate" added to the solution thus obtained. The whole

bined ammonia, the threads are formed as described above. The method of drying preferred is shown in Fig. 138, 1 being a plan view, and 2 a sectional view on line 2,2. The threads are wound on the

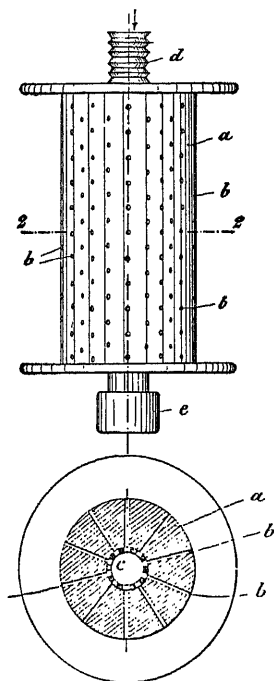


FIG. 138.—Linkmeyer Process for Manufacturing Glossy Cellulose Threads.

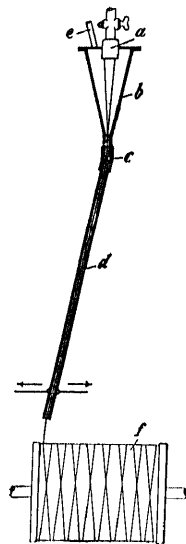


FIG. 139.—The Thiele Artificial Silk Spinning Apparatus.

cylinder *a*, *b* are radial holes, and *c* a central opening into which is fitted a pipe *d*, perforated with corresponding holes, one end being closed

mixture is then boiled and used while still hot. The incorporation of carbohydrates is proposed (U.S.P. 962770, 1910; E.P. 14112, 1909; abst. J.S.C.I., 1910, 29, 622) to increase the stability of the ammoniacal copper oxide solutions of cellulose, mannite, cane sugar or gums being recommended. For example, 400 gm. copper sulphate are dissolved in water and mixed with 240 cc. caustic soda solution of 38° Bé. strength, also diluted with water. Then 20 gm. dextrin, cane sugar or mannite dissolved in water are added. In this solution is submerged 200 gm. finely cut cotton fiber, which is afterward pressed out by a filter, the pulp containing the cupric hydroxide together with the organic substances added. This mass is then dissolved in 1000 cc. ammonia, sp.gr. 0.910. Either simultaneously with the addition of the ammonia or soon thereafter a further amount of carbohydrate may be added if necessary. The patentee claims this method produces perfectly homogeneous solutions for artificial filament production. H. Bernstein uses sugar (U.S.P. 965273, 1910) or molasses (U.S.P. 965557, 1910) for the same purpose, while V. Mertz (U.S.P. 954984, 1910) stabilizes the cuprammonium solution by the addition of sodium potassium tartrate, 1%, and glycerol, or ammonium persulphate 1-2%. Potassium or ammonium permanganate or ammonium perchlorate may also be used.

by the stopper *e*. Air injected or exhausted through the pipe *d* passes through, and dries the layers of thread wound upon the cylinder *a*.

"Cellulo" Silk is the commercial name which has been applied to the artificial filament originally developed by E. Thiele, and more recently with the assistance of W. Dreaper, and which is a modified copper-ammonia process. The apparatus (Fig. 139) for the manufacture of artificial silk according to Thiele<sup>1</sup> is characterized by the formation of the thread being effected in a freely suspended column of liquid—supported in a vessel only by the pressure of the air, the vessel being provided with a narrow opening in the bottom. The effect of this arrangement is that the precipitation bath can be under a low pressure, which can be varied, as desired, accordingly as the column of liquid is higher or lower and according to the speed at which the precipitation bath flows through, the passage of the thread through the opening being thus greatly facilitated by the low pressure. Moreover, this invention enables the thread which sinks down in the bath to be removed without the necessity of altering the direction of the thread, as must be done in those spinning vessels, which are closed at the bottom. This reversal of the direction of the thread, however, as is practiced in the ordinary spinning vessels by means of guide rollers, elbow pipes, and the like, often involves breaking of the thread and prevents the detached and falling ends of the fibers from being rejoined to the body of the thread. This disadvantage is in a measure obviated by the present invention, as the threads after running through the suspended column of liquid pass immediately outside the bath without alteration in their direction, and can be further treated—such, for example, as being wound up.

The spinning liquid enters through the rose or nozzle *a* in "thread form." The threads formed run through the funnel *b*, which is closed at the top and open at the bottom, and the funnel or delivery pipe *d*, flexibly attached by the hose coupling *c*, and are set by means of the precipitating bath contained therein. In order to renew the precipitation bath and insure a better production of threads, fresh precipitation liquid is admitted slowly through the supply pipe *e* and discharged again through the opening at the bottom of the funnel pipe *d*.

In winding the threads on the rotary drum *f* the funnel pipe *d*, which is flexibly connected with the spinning funnel, enables the threads to be slowly moved to and fro over the drum, and thus uni-

1. U.S.P. 750502, 1904; F.P. 334507, 1903. Letters Patent in Germany, dated Dec. 24, 1902, and for a design patent in Germany, dated Jan. 15, 1903, and for Letters Patent in Belgium, dated Aug. 8, 1903; in England, dated July 28, 1903; in Italy, dated Aug. 10, 1903; in Austria, dated Aug. 6, 1903; in Sweden, dated July 30, 1903, and in Switzerland, dated July 30, 1903.

formly distributed thereon. In Fig. 140 at 1 numerous filaments issue from the perforated rose-like end of the tube *a* and are considerably extended by their own gravity in passing down through the tube *b*, filled with slowly acting precipitating liquid. They are then led through the narrow connecting passage *c* into the tube *d*, which is filled with rapidly acting precipitating liquid, and after leaving *d* they are wound up in the usual way, scoured, and washed. The passage of the filaments is indicated by dotted lines on the drawings. The tubes *b* and *d* are provided with supply and discharge pipes *e f* *g h* for discharging the precipitating liquids when they have been rendered inefficient after long use, and replacing them with fresh liquids. For enabling the tubes *b d* to be cooled or heated, as may be required, they are surrounded by jackets *i k*, through which a cooling or heating fluid is made to circulate.

In the arrangement at 2 the filaments issue from the tubes *ll* and pass through the vessel *m*, filled with slowly acting precipitating liquid, into the vessel *n*, filled with the same liquid, and are wound up on the roller *o*, and

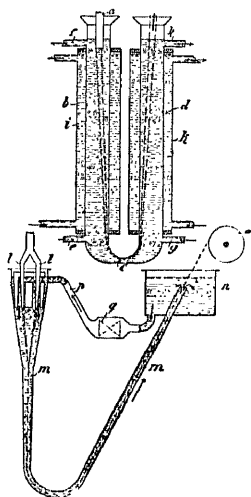


FIG. 140.—The Thiele Spinning Apparatus, Showing the Method of Winding the Filaments.

while on this they are successively treated with the rapidly acting precipitating liquid, with acid, and with water. For stretching the issuing filaments in the tube *m* there is provided between the tube *m* and tank *n* a fluid motor *q*, operating as a propeller, which drives the liquid energetically in the direction of the issue of the filaments through the tube *m*, and thereby draws out the comparatively thick filaments to any desired degree of fineness. Thiele<sup>1</sup> produced fine filaments by allowing the solutions to issue from orifices of comparatively large diameter (about 0.5 mm.), the principle being applied of reducing the diameter of the filament by rapidly drawing them away from the mouth of the orifice before they are fully dehydrated.

To obtain the requisite plasticity of the cellulose threads, the orifice is caused to discharge directly into a bath of feeble precipitating power, and when the filaments are sufficiently attenuated they are fully dehydrated by passing into a more con-

1. Thiele: U.S.P. 710819, 1902; E.P. 8083, 1902; F.P. 320446, 1902; abst. J.S.C.I., 1901, 20, 1393; 1902, 21, 25, 550. See Thiele, Mon. Text. Ind., 1897, 12, 331; Ind. Text., 1897, 13, 148; Text. Col., 1897, 19, 109; Färb. Ztg., 1897, 33, 117; Muster. Ztg., 1897, 46, 501; Text. Mfr., 1897, 23, 235.

centrated coagulating solution. The coagulating bath<sup>1</sup> is cold NaOH of 39° Bé. strength, or a hot solution of greater dilution. In the subsequent stretching of the filaments, in order to obviate the danger of the threads sticking together during the progress of precipitation, the thread is either allowed to fall through a sufficient depth of the precipitating fluid or taken up by a suitable winding apparatus.<sup>2</sup> By means of this stretching, it is claimed that a high, silky sheen is produced. The gradual coagulation of the cuprammoniacal cellulose filament can best be accomplished, according to W. Dreaper,<sup>3</sup> as follows: In the long outer tube, into which the jet of cellulose solution is discharged, a shorter, inner tube is introduced, which surrounds the jet and extends for a short distance along the path of the thread. The more dilute solution of the precipitant enters this inner tube above the jets by a supply pipe, and thus a fresh solution of constant strength is kept in contact with the newly formed thread. The more concentrated solution of the precipitating reagent is introduced into the upper end of the outer tube and flows in the same direction as the more dilute solution, with which it gradually mixes. He claims that best filaments of cuprammonium cellulose solutions are to be obtained<sup>4</sup> by the addition of organic substances which materially increase the viscosity of the solution. For example a 10% solution of glucose containing 10% of sodium hydroxide may be used for spinning with a 10–12% solution of cellulose. The temperature of the precipitating bath may be raised even up to 70°. Where such a bath is used, the cellulose or hydrocellulose is dissolved in aqueous solutions containing either zinc chloride or copper carbonate dissolved in ammonia.

In the English works of this process at Great Yarmouth it is said<sup>5</sup> yarn is being produced of a fineness of 35 denier or even lower, and in spite of its relative fineness, the number of filaments is claimed to be greatly in excess of that of other makes which are on the market at the present time.

**R. Langhans** has proposed to spin solutions of cellulose in sul-

1. Thiele; D.R.P. 173628, 1902, Addition to D.R.P. 151507, 1901; D.R.P. 157157, 1901; abst. Chem. Centr., 1905, I, 576; E.P. 15133, 16078, 1906; abst. J.S.C.I., 1906, 25, 924; E.P. 367979, 367980, 1906; abst. J.S.C.I., 1906, 25, 1144; U.S.P. 838758, 1906; abst. J.S.C.I., 1907, 26, 197.

2. Thiele and R. Linkmeyer. E.P. 16088, 1905; D.R.P. 179772, 1905.

3. E.P. 13868, 1907; see also E.P. 27222, 1905.

4. E.P. 20316, 1908; difficulty is experienced in the weaving in those composite artificial silk threads in fine counts where the thread is in a condition similar to that of "boiled off" silk. To remedy this, according to Dreaper (E.P. 11959, 1908), the threads are dried at such a tension that in the final state of the yarn the filaments stick together as in "raw" silk. In order to improve the state of the thread, it may be dried out of a solution of soluble oil or other suitable colloid.

5. Dreaper, J.S.C.I., 1909, 28, 1299.

phuric and phosphoric acids,<sup>1</sup> for which purpose cellulose is first subjected to a "purifying process" by first treating with an alkali and then with aqueous hydrochloric or sulphuric acids, afterwards washing with water until neutral, and finally drying at about 40°. The cellulose is next impregnated with a solution consisting of aqueous phosphoric acid, containing 33% of phosphorous pentoxide, and sufficient sulphuric acid so that the combined solutions contain 20%  $\text{H}_2\text{SO}_4$ , using only enough to impregnate the cellulose, which is allowed to act until the fibers begin to swell and pass into solution. The mass is then kneaded with sulphuric acid, and phosphoric acid added, when the dough is said to be transformed into a glass-like, transparent, viscid syrup, suitable for filament formation. It appears that but little commercial use has been made of this process.

**Work of E. Crumière** on ammonio-cupric cellulose commences in 1906, in which year he published a method<sup>2</sup> of treating cellulose in the manufacture of artificial silk by the action of ozone or ozonized air in conjunction with a solution of caustic soda or potash. Thus treated, it is stated, the cellulose rapidly dissolves in cuproammoniacal solution, thus giving a fluid of consistency for the manufacture of threads.<sup>3</sup> In order to remove all traces of copper from the coagulated cellulose<sup>4</sup> the material is placed in a vat which contains a liquid capable of dissolving copper, such as, for example, dilute sulphuric or acetic acid. An electric current is then passed between two suitable metallic electrodes which are immersed in this liquid. The vat itself can be used as the cathode. The copper contained in the cellulose is dissolved and then deposited on the cathode. For the purpose of this treatment the coagulated cellulose may be either wound on bobbins or arranged in the form of hanks.

The filaments, after formation, are coagulated by passing into a bath of potassium or sodium zincate prepared by adding sodium or potassium hydroxide to a zinc salt until the precipitate first formed just dissolves.<sup>5</sup> The copper remaining in the coagulated cellulose may be eliminated<sup>6</sup> by passing an electric current through a solvent in which the coagulated cellulose is immersed in such a manner as to dissolve the copper and deposit it on the cathode.

1. U.S.P. 571530, 1896; D.R.P. 72572, 1891; 82857, 1893; F.P. 217557, 1891; Text. Col., 1897, 19, 317; Ind. Text., 1897, 13, 239.

2. F.P. 361048, 1905; E.P. 22422, 1906; U.S.P. 908754, 1909.

3. It is recommended to add metallic copper to the ammoniacal solvent, for the purpose of reacting with the ammonia liberated, and of replacing in it the "copper" absorbed by the cellulose during the first stages of its action upon the latter.

4. F.P. 377118, 1907, and First Addition thereto, dated Mar. 17, 1908; abst. J.S.C.I., 1907, 26, 1045. See also F.P. 415003, 1910.

5. F.P. 375827, 1907.

6. E.P. 2794, 1908.

**Ernst Friedrich**<sup>1</sup> claims that by using an alkylamine as solvent for copper hydroxide instead of ammonia, it is possible to obtain more concentrated solutions of cellulose, and that the solutions so obtained are more viscous and less liable to deterioration on standing. It is stated that the coagulation is done very quickly, the resulting filament being so resilient that broken threads rarely occur, and that the thread, therefore, may be wound up with a high speed, and finally can be very easily washed, owing to the high solubility of the alkylamine in water. The process is carried out by dissolving cupric oxide alkylamine with cellulose in the following manner: 320 gm. of well-cleaned cellulose is moistened with hot water, pressed, and while still wet mercerized with 3,400 cc. NaOH, of 30° Bé. strength. The mercerization being finished, 250 gm. powdered copper sulphate is added gradually, the sodium sulphate formed by interaction separated by filtration, and the wet mass remaining triturated with a 30% solution of monomethylamine or monoethylamine in water, any elevation in temperature being avoided. The mass first gelatinizes and later dissolves. The alkylamines resulting from beet-sugar and molasses manufacture are claimed to be applicable and are readily procurable in large amounts. The solution is spun in the ordinary way.

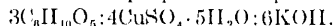
In a subsequent process<sup>2</sup> the preparation of a solution of cellulose is described in which much less ammonia (about one-half) is required than hitherto was considered necessary.<sup>3</sup> Best results are obtained<sup>4</sup> with cellulose compounds prepared by subjecting cellulose to the action of either an oxidizing agent, caustic soda, or an acid (sulphuric acid of 50° Bé.).

The work of E. Friedrich above is not to be confused with that of Philipp Friedrich, the latter having devised a process<sup>5</sup> in which

1. U.S.P. 813878, 1906; F.P. 357171, 357172, 1905; E.P. 17381, 1905; 6072, 1906; abst. J.S.C.I., 1906, 25, 88.

2. U.S.P. 850571, 1907; E.P. 27727, 1906.

3. The following example illustrates the invention: Basic copper sulphate is precipitated upon 50 gm. of hydrated cellulose by mixing hydrated cellulose, copper sulphate, and caustic potash in the proportions represented by the formula:



The cellulose thus prepared is divided into four equal portions. Of these one is dissolved in 250 cc. of ammonia solution of sp.gr. 18° to 20° Bé. To the solution thus obtained the other three portions are added little by little, and at the same time there is added in all 250 cc. of the same solution of ammonia distributed between the separate portions of cellulose, the portion of ammonia solution added being more strongly diluted with water for each successive portion of cellulose and the total quantity of water added being sufficient to bring the total volume of the liquid to one liter. It is necessary to observe that the proportion of water to solution of ammonia in the last portion added should be 1:1 to 1:1½, because if a more dilute solution of ammonia were used coagulation might ensue. The solution thus obtained is filtered, for which purpose a metal gauze having 160-180 meshes to the centimeter will suffice.

4. F.P. 364066, 1906.

5 D.R.P. 206883, 1907.



solutions containing 6% of cellulose are forced through suitable orifices into a coagulating bath consisting of 25 k. sodium chloride and 4.5 k. sodium hydroxide in 100 l. of warmed water. In a subsequent method<sup>1</sup> aluminum, calcium and magnesium chlorides are advocated as preferable precipitants to sodium chloride and hydroxides.

**Animal Silk** is the generic name given to certain gelatin, glue and casein compounds, which more nearly approach the term "Artificial Silk" than the foregoing, inasmuch as they are—like natural silk—structureless, of animal origin, and can be transformed directly from a fluid to solid state without the use of a coagulating medium other than air. They differ from natural silk, however, in being less brilliant and much weaker when wetted, and also have the disagreeable property of swelling in moist atmosphere from absorption of water, and possess a comparatively high degree of brittleness. Gelatin silks dissolve rapidly in acids and alkali hydroxides, and on calcining—like natural silk—burn with characteristic odor of burnt feathers or horn, and the evolution of alkaline vapors; cellulose silks burn without odor, and with the evolution of acid vapors. Like the natural fiber, the fiber of cellulose silk swells in contact with

1. E. P. 17967, 1908; 7617, 11700, 14112, 28256, 1909; F.P. 404372, 1909, and First Addition thereto, dated Mar. 23, 1909; abst. J.S.C.I., 1909, 28, 1246. According to his E.P. 4104, 1909 (abst. J.S.C.I., 1909, 28, 934) carbohydrates or gums were added to the solutions of cellulose. Solutions having the same properties can be more directly obtained by preparing the cellulose solutions from those plants which contain both carbohydrates and cellulose. The outside layers of the rice plant, it is claimed, give good results if they are first treated with alkalis and then bleached and washed before being dissolved in the cuprammonium solution. Mannitol (E.P. 14112, 1909) is said to improve the keeping properties of a cuprammonium solution. In a subsequent patent (F.P. 409789, 1910; E.P. 28259, 1909) he manufactures artificial threads using cuprammonium cellulose solutions of great tenacity, as, for example, those containing, in addition to cellulose, such substances as carbohydrates or alcohols, as described in F.P. 400321 (E.P. 4104, 1909), and addition thereto (J.S.C.I., 1909, 28, 934, 1121) and F.P. 404372 (E.P. 11700, 1909; J.S.C.I., 1909, 28, 1246), filaments squirted in the usual manner may be drawn out into very fine threads and hardened in a single coagulating bath, preferably of the kind described in D.R.P. 206883 (abst. J.S.C.I., 1909, 28, 362). The cellulose solution should contain a smaller quantity of ammonia than of cellulose, and it should have such a tenacity that it can be drawn into filaments 50 cm. long in the air; the concentration of the coagulating bath should be so adjusted that the filament can be drawn out without breaking during the first 10 cm. of its passage through the bath.

He prepares (F.P. 410882, 1909) a hydrated basic copper salt intended specially for the solution of cellulose, having found that in the precipitation of copper as hydrated oxide, a certain amount of alkali carbonate is introduced; this gives a product, by means of which the solution of cellulose can be readily effected with very little ammonia. For example, to 370 gm. of powdered crystallized copper sulphate, dissolved in 2 l. of water, are added, 130 cc. of sodium hydroxide solution (40° Bé.), diluted with 1500 cc. of water; 25 gm. of sodium bicarbonate, dissolved in water, are next introduced and then a further 45 cc. of sodium hydroxide (undiluted). The precipitate is mixed with 200 gm. of finely divided cellulose, and the mixture, pressed as dry as possible, worked into a filament 1 m. long with 600 cc. of ammonia (sp.gr. 0.888). On adding 48 cc. of ammonia solution the whole immediately dissolves, forming a viscous solution, said to be very suitable for the manufacture of artificial silk.

water, but, on the contrary, contracts in alcohol or glycerol. With Fehling's solution the fiber is colored a violet, iodine and sulphuric acid yield a yellow or brown, chloriodide of zinc a yellow, and Vetillard's reagent a red coloration which disappears on washing.

**Vandura Silk** is obtained by the use of gelatin as a basis, which is rendered insoluble after being formed into filaments by exposure to formaldehyde vapor, and was so named by the patentee, the late A. Millar. A concentrated solution of gelatin is first prepared, carefully clarified from insoluble albuminous particles, melted by heat, and forced through spinnerets on to an endless traveling band, sufficiently long to permit of thorough drying of the threads. The latter then pass into a closed chamber where they are subjected to the action of dry formaldehyde vapor.<sup>1</sup> The process of Hummel of Leeds, is essentially the same. On account of the partial solubility of the formaldehyde gelatin in water, it cannot be dyed after formation into threads, but must be colored in the melted state before spinning. The wool and silk acid dyes are suitable for dyeing gelatin.<sup>2</sup> The brittleness may be partially overcome by the introduction of 5-20% castor oil, glycerol, or similar softening agent. In the process of L. Jannin<sup>3</sup> gelatin 1 k. in water 1 k. and glycerol 100 gm., containing

1. Millar describes his process as follows (U.S.P. 594888, 1897; 625315, 1899; 611814, 1898; E.P. 15522, 1894; 2713, 1897; 6700, 1898; D.R.P. 88225, 1895; 93795, 1897; Sw.P. 12728, 1896; 18012; F.P. 248830, 1895): Four lb. of the best gelatin is broken up into granular pieces such as will pass through a 16 mesh sieve. It is then placed in a melting vessel with 2 lb. of cold water added, stirred well and left to stand for one hour. The vessel is next placed in a can of hot water and kept heated for another hour, stirring once or twice. By the end of the second hour the solution of gelatin is of uniform consistency, containing 66% of gelatin.

The group of filaments are next twisted together and spread out in a thin layer on an open metal reel, about a foot in diameter. A number of these reels of plain gelatin yarn are now placed in a chamber in which a very small quantity of formaldehyde has been poured, and is therefore filled with formalin vapor about 80 minims of formalin to a space of 10 cubic feet. An exposure to this vapor at ordinary temperature completely changes the gelatin. It is no longer soluble, even in boiling water, and has a splendid luster.

The reels are hung up to allow all smell of the formalin to disappear, and the artificial silk is finished, needing only to be wound on bobbins for the convenience of handling before it gets into the hands of the textile manufacturer.

The nipples of the machine had a bore of 0.01 inch, but the filaments drawn from these nipples may be only 0.001 inch in diameter. The flow of the liquid through the nipples is regulated by air pressure. An India rubber pipe leads from a receiver of compressed air, and has its other end attached to a small pipe fixed to the air-tight cover of the cylinder which contains the gelatin solution. The endless traveling band, on which the threads fall, and by which they are drawn away rapidly, moves at a uniform rate—say 60 yards per second; but if the speed be increased to 120 yards, the filament would be twice the fineness; the same result is obtained by reducing the pressure in the air receiver or reservoir. See also C. Miller, J.S.C.I., 1900, 19, 326.

2. H. L. Chavassieu (F.P. 395402, 1907, and First Addition thereto, dated Nov. 28, 1908) renders the filaments more supple and elastic by treating them with 2-5% solutions of quinone or quinol (hydroquinone).

3. F.P. 342112, 1904; see C. Dye, D.R.P. 106293, 1898, for a similar process.

1-2 gm. formaldehyde per liter, is forced through spinnerets at 80-100°, and afterwards into a mixture of alcohol or acetone and formaldehyde to harden the fibers. In order to more closely approximate the appearance and composition of real silk, H. Bernstein has patented the novel process<sup>1</sup> of utilizing with the gelatin the liquor resulting from the treatment or boiling of raw silk, it being claimed that the final product obtained is more pliable, elastic, and lustrous, and does not shrink or shrivel as readily from moisture or other atmospheric changes.<sup>2</sup>

**Bichromate Silk** is similar to Vandura Silk, with the exception that the glue or gelatin, instead of being rendered insoluble by the action of formaldehyde, is treated with potassium bichromate with subsequent exposure to light, whereby the gelatin takes on a light-green color from the reduction of bichromate to normal chromate, and at the same time becomes nearly insoluble in water. Bichromate equal to about 2% of the weight of the gelatin is used. Sodium bichromate, on account of more ready solubility in water, has been considered as preferable by some. A. Helbronner and E. Vallee<sup>3</sup> have described a process of producing textile threads by treating ossein obtained from bones by digestion with dilute alkali and forcing this solution into filaments. M. Gérard<sup>4</sup> combined 5 parts of 30% gelatin (in acetic acid) with 10 parts of 30% nitrocellulose in the same solvent, producing threads which have, as yet, reached no industrial importance.

**Casein Silk**, or the artificial fibers formed from the coagulable portions of milk, were first described by F. Todtenhaupt<sup>5</sup> in his E.P. 25296 of 1904. The casein is first dissolved in an alkali solution, which is then passed through forming nozzles into a dilute acid bath; the threads thus formed are stated to be insoluble and very tough,

1. U.S.P. 712756, 1902; 798868, 1905; in which he takes 6½ parts of gelatin and 3 parts of the liquor resulting from boiling raw silk. These in cold condition are placed in a suitable tank for about two hours, and stirred, so as to be thoroughly mixed. The resultant body is then introduced into another vessel and subjected to heat of about 50° for an hour, after which the mass is placed in an air-tight vessel provided with nozzles or orifices and subjected to pressure, whereby it is forced through the nozzles in the form of filaments, which, drying rapidly, are twisted into threads and wound on bobbins or formed into skeins. These are now subjected to the vapor of formaldehyde in order to render the material insoluble, after which it is ready for use.

2. The composition for manufacturing artificial silk of H. Turk (U.S.P. 563214, 1896) consists of nitrocellulose 96, gelatin or isinglass 2, dissolved in glacial acetic acid, 1,600 (all parts by weight).

3. E.P. 20548, 1908; Hüschler (D.R.P. 179833, 1907) also employs ossein for the same purpose.

4. D.R.P. 40373, 1886.

5. Todtenhaupt, D.R.P. 203820, 1907; Addition to D.R.P. 170051; F.P. 356404, 1905.

and to contain 15–16% nitrogen. The alkaline casein solution is prepared by dissolving 1 part of casein in 3 parts 10% aqueous ammonia and 4 parts water. The fibers obtained by this process, however, contain so much water that they readily adhere together, which has been obviated in a subsequent process<sup>1</sup> by employing pure casein, which dissolves in water to a fairly clear solution. This is converted into a thick solution by dissolving in alcohol 80 and water 20 (parts) in the presence of traces of bases or salts. The solutions thus formed are said to contain 1 part of casein to 1.5 parts of solvent, and to be sufficiently viscous to form into threads which do not adhere, and without the necessity of precipitation by acids. Solutions of the casein in zinc chloride,<sup>2</sup> methyl alcohol,<sup>3</sup> and formaldehyde<sup>4</sup> have been advocated as precipitating agents. O. Nowak<sup>5</sup> dissolves the casein by aid of 5% of dioxynaphthylmethane, and H. du Boistesselin and C. Gay<sup>6</sup> by excess of soda lye. H. Cathelineau and A. Fleury<sup>7</sup> dissolve the casein in a phenol (e.g., carbolic acid, creosote or guaiacol) and then add cellulose nitrate before spinning.

In the process of H. Timpe<sup>8</sup> casein or paracasein is dissolved in an alkali (either ammonia or caustic soda), acetone is added, and the mixture heated until frothing commences. After standing for some time the precipitate formed is removed, and the liquid evaporated, which soon sets to a solid mass upon cooling. This is rendered plastic on heating, and in this condition is worked into threads which are rendered insoluble by treatment with formaldehyde vapor. In still another method,<sup>9</sup> an acetic acid solution of casein is given the requisite viscosity for spinning into filaments, by incorporating a glacial acetic acid solution of nitrocellulose. Gelatin and casein have been combined as in the process of Foret.<sup>10</sup>

The spinning processes described do not differ essentially from those used to form filaments of nitrocellulose. It appears that the same defects in the filaments noted under gelatin and glue silks are present with casein filaments, and so far as the author is aware, these products are not commercial articles at the present time.<sup>11</sup>

1. Todtenhaupt, D.R.P. 203820, 1907; Addition to D.R.P. 170051; F.P. 356401, 1905.

2. *Ibid.*, F.P. 356504, 1905; abst. J.S.C.I., 1905, **24**, 1063.

3. *Ibid.*, D.R.P. 183317, 1906.

4. *Ibid.*, U.S.P. 836788, 1906.

5. U.S.P. 809371, 1906.

6. F.P. 403193, 1909.

7. D.R.P. 185240, 1906.

8. F.P. 356508, 1905.

9. Process of H. Dunham, U.S.P. 748709, 1904.

10. F.P. 361759, 1905.

11. See also Casein Plastics.

**Incandescent Electric-Light Filaments.** Lane-Fox was probably the first person to patent (England) a carbon filament. He used "vulcanized fiber," which is cellulose partially parchmented by zinc chloride and afterwards formed into shape mechanically. J. Swan<sup>1</sup> worked out the same idea quite independently, both with zinc chloride and parchmentizing by the aid of sulphuric acid. In the latter method the acid is first diluted with water to 1.64 sp.gr., the thread in very loose form being used. For ordinary 50 volt lamps, knitting cotton was found to be the best. The action of the acid is prolonged until the cotton appears gelatinized, and until a point is reached where, if the action is continued much longer, the cellulose would entirely disintegrate. If on the other hand the structure of the cotton is not sufficiently acted upon, the filament does not give uniform results. W. Crookes patented the use of Schweitzer's reagent, in which he proposed to dissolve cellulose in cuprammonium solution in a method similar to that described under "Glanzstoff". E. Weston of Newark, N. J., was the first to use pyroxylin in this industry, his patent being granted in 1882.<sup>2</sup> Weston first nitrated cotton and dissolved this in ether-alcohol, poured into shallow vessels to dry, after which the films were cut up into thin strips and denitrated. Weston's fluid cellulose nitrate solution, called "tamaline," was used in the patented method of J. Swan,<sup>3</sup> who forced the solution—often containing acetic acid—through small nozzles by compressed air into alcohol as the coagulating medium. E. Oberle<sup>4</sup> first prepared a 50% solution of thorium oxychloride in alcohol, which was subsequently mixed with a 3–20% solution of nitrocellulose in ether-alcohol if the thread was to be spun with air pressure.<sup>5</sup> The threads after formation, washing and drying are ignited in the air and after decomposition, the salts are changed into oxides by ignition in a Bunsen burner.

F. Wynne and L. Powell<sup>6</sup> used, in addition to the chlorides, bromides

1. E.P. 4933, 1880. See A. Parkes, E.P. 983, 1881; F.P. 144257, 1881; Belg. P. 55383, 1881; U.S.P. 257607, 1882.

2. U.S.P. 264987, 1882; E.P. 4458, 1882.

3. Fitz Gerald also patented in England the use of zinc chloride for carbon filaments, and J. Hoyne (U.S.P. 625033, 1899) the same in the United States. See E. Bronnert, E.P. 18260, 1899; F. Ahrens, D.R.P. 216629, 1907.

4. E.P. 3029, 1884 (abandoned). See J. Swinburne, London Electrician, 1887, 18, 60, 98, 121, 187, 255, 286, 303, 323, 346, 368, 418, 462, 496, 539. In the patent of Wynne and Powell (E.P. 16805, 1885), zinc was dissolved in dilute HCl in the presence of an excess of zinc until effervescence ceased, zinc carbonate in excess being added to neutralize excess of hydrochloric acid, the liquid filtered and evaporated. When cotton cellulose was stirred in this liquid and heated a mass soon resulted. W. Dreaper converts cellulose into . . . (U.S.P. 1908) and then dissolves the latter in zinc chloride.

5. E.P. 15556, 1896, abst. J.S.C.I., 1897, 16, 603.

6. E.P. 16805, 1885, abst. J.S.C.I., 1886, 15, 172. The oxychloride may be

and iodides of zinc or bismuth, precipitating the formed filament by alcohol, ether or acetic acid. O. Knöfler<sup>1</sup> succeeded in making from collodion endless impregnated threads, by charging the pyroxylin with salts of incandescent oxides, and operating in a manner similar to that used by Chardonnet in the formation of artificial filaments.<sup>2</sup> The pyroxylin solutions are usually denitrated with ammonium sulphide, ferrous sulphate or chloride or other reducing agent, the regenerated cellulose thus obtained being used for filaments as above. In addition to electric-light filaments, microphone carbons and the spider hairs in surveying instruments are obtained from this source.

**Artificial Horsehair, Gorse, Whalebone, Hemp, Lint,** and analogous fibers have been made from regenerated cellulose, and especially nitrocellulose. In the method for forming artificial whalebone patented by Knight<sup>3</sup> metal strips are coated with a mixture of nitrocellulose and India rubber, the resulting product, it is stated, being not liable to crack and split, as with the natural bone. In another method a plurality of bast fibers are coated with pyroxylin of high viscosity and then formed by mechanical means into a flattened

satisfactorily spun, the inventor claims, when as low as one-fourth part of nitrocellulose is present. The proportion of alcohol must exceed that of ether, it was found, if the thread is to be spun under water in a homogeneous solution, because ether precipitates thorium oxides or a basic salt. The spinning may be effected with either a weak or strong solution. In the former case the solution is passed through glass tubes with capillary openings immersed in water in which the alcohol and ether readily dissolve, the thread being dried in the air. In the latter case, the solution, consisting of 20% nitrocellulose and 80% thorium oxychloride dissolved in alcohol and ether, is passed under pressure into the open air.

1. E.P. 11038, 1895; abst. J.S.C.I., 1895, 14, 797. For "cupricellulose incandescents," see A. Müller, Zeit. ang. Chem., 1906, 19, 1810; Bruno, Ibid., p. 1387.

2. The collodion is mixed with an alcoholic solution of the salts to be employed or with the solid oxides of salts soluble in alcohol. After forcing the mixture through a series of capillary tubes, and the resulting filaments are coagulated by passage through a solvent which will dissolve the alcohol and ether of the pyroxlin solution without attacking the inorganic salts evenly distributed throughout the thread. Water is the simplest and cheapest fixing agent, which, if rendered alkaline, will immediately cause a coating of oxide to be formed on the thread, which will be thus protected from the solvent action of the water. Since the combustion of such threads is so energetic as to partially disrupt the filaments, they are first denitrated. If the filaments are to be used for incandescent mantles, they are woven as in the usual method of formation. Mantles woven from such impregnated pyroxylin filaments are much more durable than those woven from cotton threads and subsequently impregnated, the advantage accruing from the smaller percentage of ash in pyroxylin than in cotton, which is very detrimental to the light-emissive power of the finished mantle. See P. Follet and G. Ditzler, D.R.P. 223294, 1907; addition to D.R.P. 211871, 1906; Hanauer Kunstseidefabrik, D.R.P. 222873, 1908; R. Pawlikowski, D.R.P. 222624, 1908. See Chapter X.

3. E.P. 1765, 1890; abst. J.S.C.I., 1891, 10, 264. One of the disadvantages of natural horsehair when used in the arts, as for bordering, trimming, or embroidery, is that the shortness of the individual hairs requires that they be united or spliced, so as to form a continuous thread adapted for uninterrupted work.

strip, with a holder stitched or cemented on.<sup>1</sup> According to Müller<sup>2</sup> the incrusting substances of Mexican grass are first removed by boiling the grass for about two hours in 1-2% NaOH solution, being then washed and dried, after which they are superficially parchmented by immersion in strong sulphuric acid or zinc chloride solution. By now coating these fibers with a pyroxylin solution, they are stated to assume a hair-like character, possessing great elasticity and strength, and to be especially adapted for the production of artificial whalebone.

The name "Artificial Horsehair" has been applied to those filaments of 300-400 deniers size, which, while resembling silk in appearance, are approximately of the diameter of natural horsehair. It is evident that by enlarging the spinneret apertures, larger filaments may be produced, but there is a well-defined limit, above which it is not advisable to produce a single thread. When the diameter of the thread exceeds a certain size, the volatilization of the contained solvents and the regeneration of cellulose in denitration do not proceed uniformly or satisfactorily. For the production of uniform threads of greater diameter, spinnerets with the maximum orifice to produce satisfactory threads are used, and a number of spinners are so placed that the filaments emerging from them touch before the contained solvent has had an opportunity to evaporate, the result being that the several filaments adhere and coalesce into one thread. In order to increase the adhesion, the filaments may be passed directly from the spinners into a weak acetone solution, which will sufficiently dissolve the nitrocellulose filaments to cause them to firmly adhere to each other. From this they are passed into a bath of water which removes the alcohol, ether and acetone, and finally the combined filament is dried and perhaps dyed. In this manner it is commercially practicable to produce individual hairs exceeding in diameter that of horsehair. In Lehner's method<sup>3</sup> the coalesced fibers are com-

1. For method of producing artificial hemp lint by artificial silk see Vereinigte Kunstseide-Fab. Akt.-Ges. Kolster & Co., D.R.P. 184510, 1906.

2. E.P. 3725, 1890; abstr. J.S.C.I., 1891, 10, 539.

3. U.S.P. 713999, 1902; E.P. 17759, 1900. The individual fibers or strands of the material used for this purpose must be sufficiently softened so as to disappear to such an extent that the inner microscopic structure of the same disappears and the separate fibers merge into a single or integral filament without spaces or intervals. The liquid used to congeal the fused threads depends on the starting material and the solvent bath employed. Where an ammoniacal copper oxide solution has been employed as a solvent, an acid such as sulphuric or acetic acid, etc., is used; where zinc chloride was used as a solvent alcohol is to be employed as a congealing agent, when sulphuric acid was the solvent water should be the congealing agent, where nitrocellulose and ether or alcohol have been employed a mere exposure to the air or drawing the filament through water will be sufficient to arrest the solvent action. Thereupon the solvents and the congealing substances are completely removed from the filament by washing in much water, and the product dried on reels. In order to correct any flaws resulting from the imperfectly

pacted by drawing, and then passed through a hardening bath. Fine threads of silk, cotton or linen may be used as the filling substance of these artificial hairs, as in the process of F. Schauman and A. Larsson,<sup>1</sup> where the threads are immersed in an alcohol-ether solution of nitrocellulose containing 16 gm. per 100 cc. It is preferable to add to the solution 5-15% shellac and also 3-4% castor oil to increase the elasticity of the product. After coating, the threads are immersed in warm water to remove the solvent, denitrated if desired, and dried. The product is said to closely resemble natural horsehair, being stiff, but not brittle. The stiffness may be varied within wide limits by the use of varying proportions of castor oil. The processes of A. Samuel<sup>2</sup> and J. de Sauverzac<sup>3</sup> differ only in unimportant particulars from the above. In the author's experience a close imitation of natural black horsehair is possible by taking 50s six-cord black thread which has not been waxed or polished and previously extracting with acetone or wood alcohol to remove any possible oil or wax, and thus cause the nitrocellulose to permeate the thread more readily. In slowly passing such thread through a pyroxylin lacquer of 12-14 oz. pyroxylin to the U.S. gal. the first coating will cause an increase in weight after drying of about 60%. A second coating applied similar to the first will cause the original thread to increase in weight about 145%. As this size thread is readily procurable in 12,000 yard spools, the coating of the thread in this manner is not a tedious operation. Thread thus coated, while still black, yet has that peculiar superficial transparency due to the colorless pyroxylin which is so noticeable in natural horsehair. Silk fish lines coated in this manner, only dyeing the pyroxylin a light green by means of victoria green dye, produces a line which is impermeable to water, nearly invisible in the water and which has a tendency to float, an advantage when using live bait, as it tends to keep the bait toward the surface and hence free from weeds and other obstructions in the water. Coating of silk line in this manner renders it very easy to reel and prolongs its life and wearing qualities. Where cuprammonium threads are used, they are immersed<sup>4</sup> while still containing copper, into a concentrated solution of sodium carbonate containing 2-6% ammonia; it is stated that under this treatment the material acquires considerable elasticity,

united strands of the components of the artificial horsehair where they have not been perfectly united without again drawing the product through the solvent and congealing bath, the artificial horsehair may be finally drawn through a solution of caoutchouc or gelatin or collodion. This will suffice to cover any such flaws.

1. F.P. 333246, 1903.

2. F.P. 348137, 1904.

3. F.P. 349620, 1904.

4. F.P. 351206, 1906; D.R.P. dated Nov. 24, 1904.



tenacity and transparency. It is then washed and freed from all the copper it contains and finally dried under tension.<sup>1</sup> In textile industries such threads are used for the preparation of the warp for especially strong fabrics, and to give the woven fibers added rigidity, so that there will be no tendency to slide out of their position. C. Roux<sup>2</sup> dips the stiffened fabric into a weak pyroxylin solution, which partially softens the fibers and causes the whole to blend into a single piece of cloth intertwined with nitrocellulose filaments. Artificial horsehair has been used as incandescent electric-light filaments, and, when knit into "stockings," for Welsbach mantles.

A. Dubois<sup>4</sup> has devised a peculiar process for giving a lisle-thread finish to fabrics by impregnating the fabric with an acid aniline black mixture, which tends to carbonize the filamental fuzz on the surface, then rolling the article in a tumbling drum until the fuzz has been removed, when the material is given a light coating of pyroxylin, which

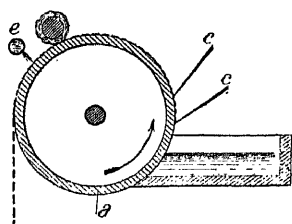


Fig. 141.—The Ratignier & Pervilhac Artificial Lace Machine.

serves the double purpose of laying the fuzz and adding luster. Artificial lace is produced by W. Ratignier and H. Pervilhac<sup>4</sup> by a method in which the pattern (Fig. 141) to be produced is engraved upon the metal or ebonite cylinder *a*, the grooves being equal in width and depth to the filaments to be produced. The trough *b* contains the fiber substance, which, as the cylinder revolves, is deposited in the engraving. The doctors, *cc*, remove any excess, and the roller *d* and the blower *e* supply the necessary hard-

1. F.P. 351207, 1905. Verein. Glanzstoff Fab. Act.-Ges.

2. F.P. 392179, 1908; R. Freerichs (U.S.P. 729749, 1903) makes artificial human hair by producing a colored cellulose fiber of suitable thickness made from cellulose solution in copper ammonia, and treating with an alcoholic solution of an oil and powdered talc. G. Kraemer (E.P. 26201, 1905; U.S.P. 912395, 1909) impregnates textile fibers with a mixture of nitrocellulose, chlorhydrins, and with aromatic sulfo acid derivatives. A suitable mixture is said to result upon combining 100 parts pyroxylin in 450 parts alcohol and 350 parts acetone, with 50-60 parts dichlorhydrin and about 25-45 parts of an aromatic derivative of a sulfo acid, as *p*-toluolsulfo chloride. The threads, fibers or fabrics are impregnated with the mixture in any suitable manner, and dried. If they are to be dim, they are simply air-dried or wind-dried, but if they are to receive a brilliant luster, they are dried by means of warm pressing cylinders, plates or rollers. Tensile strength tests show that fibers impregnated in this manner gain materially in strength. Fabrics obtained by spinning and weaving such impregnated filaments are useful for borders and hem laces on women's clothes, which owing to their impermeability to water, can be washed off any time, while permanently retaining their silky luster.

3. U.S.P. 723147, 1903.

4. E.P. 13518, 1907. The Soc. Anon. des Celluloses Planchon (F.P. 410721, 1909) prepare artificial foil by converting artificial hair into foil, by passing between rollers such as are used in the preparation of metal foil.

ening agents to the fiber substance before it leaves the engraved cylinder. The hardening agents vary according to the viscous substance used.

The speed is regulated so that the tissue can be produced continuously. The preparation of acceptable artificial bristles has been often attempted, but as yet without satisfactory results. It appears to be very difficult to combine elasticity, resiliency and wearing qualities when the bristles are wet, as when they are placed in brushes intended to be afterwards used for scrubbing. Artificial horsehair is used in large quantities in braid, passementerie, hat trimmings, chiefly the so-called "theater hats," plumes, and the ornamenting of the bodices of ladies waists with pompons, and similar decorations. A machine similar to that used for forming horsehair into fabrics, as in the old-fashioned horsehair couches, is used for this work.

"Crinol" is the French name for an artificial horsehair prepared from cuprammonium cellulose,<sup>1</sup> in which the ammoniacal cupric hydroxide is separated by hydrolysis from the other constituents of the cuprammonium solution, and this purified product used to dissolve the cellulose. The patentees claim that when all the cupric hydroxide in a cuprammonium solution is in the colloidal state, approximately two parts of cellulose can be dissolved by each part of cupric hydroxide in solution. These colloidal solutions can be prepared in two ways: (a) By treating solutions of copper salts with ammonia and caustic alkalis, the solutions being of such concentrations that the cuprammonium solution contains no more than 15 gm. of cupric oxide per liter. (b) By the joint action of air and ammonia on metallic copper in the cold and subsequent dialysis of the product. Pure cellulose is dissolved in liquor *a*, to which has been added enough of liquor *b* to make the mixed solutions sufficiently concentrated to dissolve the amount of cellulose required for the filament to be made. The concentration of the caustic alkali solution (employed in the coagulation of the solution of cellulose in cuprammonium hydroxide) is of importance, it having been found that with a low concentration the coagulation is not complete; with too strong a solution, however, the thread, after formation, tends to become brittle and is irregular in form owing to the capillary tubes of the spinneret becoming blocked. The latter faults are obviated by adding sodium carbonate to the bath (which should contain 50% of caustic soda and 25% of sodium carbonate) and maintaining the temperature of the same at about 35°. The

1. Soc. Anon. Le Crinoid, F.P. 362986, 1906; 401741, 1908; 410827, 1909; E.P. 21191, 1908; 22413, 1909; F. Beltzer, Mon. Sci., 1908, (4), 68, 657; abstr. J.S.C.I., 1906, 25, 808; Zeit. ang. Chem., 1910, 21, 1731.

threads are passed through a second, weaker bath and then through a solution of sodium bisulphate (to remove the excess of copper hydroxide), after which they are washed and dried.

"Meteor" is also a patented name for a similar article.<sup>1</sup>

**Spinning Artificial Filaments.** In addition to the spinning methods heretofore described, various refinements have been devised, especially within the past five years. In one method<sup>2</sup> the solution is supplied to closed reservoirs, one of which is discharged while the other is being charged. The discharge is effected by means of air, compressed by a pump so arranged that the pressure is accurately governed by means of weights and regulating springs which move levers connected with the electric motor driving the pump. The solution is thus delivered under pressure to a special pump fitted with several pistons in order to avoid pulsations, and especially constructed suction-valves which are under control. The pump passes the solution into a regulating cylinder containing a piston which acts as the governor for the spinning system. This piston is worked by a motor controlled in a manner similar to that working the air pump, and the pressure-accumulator is capable of very delicate adjustment by means of reservoirs of water above the weights. The process of A. Lumière et Fils<sup>3</sup> has for its object the saving of all loss of time

1. For hardening various artificial silks by means of moderately concentrated sulphuric acid solution, see Verein. Kunstseidefab. Frankfort, Text. Rec., 1903, 26, 128; Text. Mfr., 1903, 29, 299.

2. Process of Soc. Desmaris, Morane and M. Denis, F.P. 342655, 1904. In the apparatus of L. Morane (F.P. 410267, 1909; E.P. 24707, 1910), the spinning nozzles are arranged in two rows in partly rectilinear chambers, the number of nozzles in each chamber being the same as the number of filaments to be wound together on a bobbin to form the thread. Each chamber may be pivoted at one end so that the nozzles can be brought close to the workman for repairs, etc. The collodion enters the chamber through a filter at the pivoted end, the supply being regulated exactly by means of a suitable valve. To assist in the regulation, a portion of the supply tube for the collodion is formed of a piece of thick glass tubing, and immediately in front of this glass tube drops of colored collodion are injected into the main supply of collodion, a color being used which is destroyed by the bath subsequently used for treating the threads. In the method of F. Coehius (E.P. 9017, 1903) abstr. J.S.C.I., 1903, 22, 1083) the liquid is forced horizontally through a number of forming-nozzles, placed in a wall of a long trough which contains the coagulating liquid. As the threads reach the further end of the trough, they are united into a single thread, the cocks for controlling the supply of liquid to the forming nozzles being regulated by a single movement. In the Hömberg process, high gloss of the filament is said to be produced by the use of jagged nozzles.

3. F.P. 350288, 1904; 361960, 1905; in this firm's D.R.P. 177957, 1905, there is described a process of manufacturing cellulose threads from nitrocellulose solutions, with a view to removing the objections to the dry setting, which renders the product apt to split, and to the wet setting, which on account of the superficial setting alters the shape and size of large threads such as artificial horsehair, consisting in bringing the thread as it issues from the nozzle into contact with a nitrocellulose solvent to which has been added, in a determined quantity, other fluids which render the solvent incapable of dissolving the nitrocellulose, e.g., methyl alcohol with 5-8% water added. The use of water for operating the hydraulic piston in the apparatus in which the collodion is supplied to the spinning device

and material which results when the spools are changed in the spinning. During the change of the bobbin a certain length of thread is lost, and the fixing of the thread to the new bobbin is one of difficulty. The apparatus works in such a way that the full spool or bobbin is removed, and at the same time stopped from revolving, while a new bobbin is put in its place and made to revolve. Fig. 142 is a vertical section of the apparatus, which consists of a double-flanged driving cylinder, which is fitted with a framework holding empty spools so arranged that the spool at the top automatically falls into gear with the driving cylinder, and commences to wind the thread upon itself.

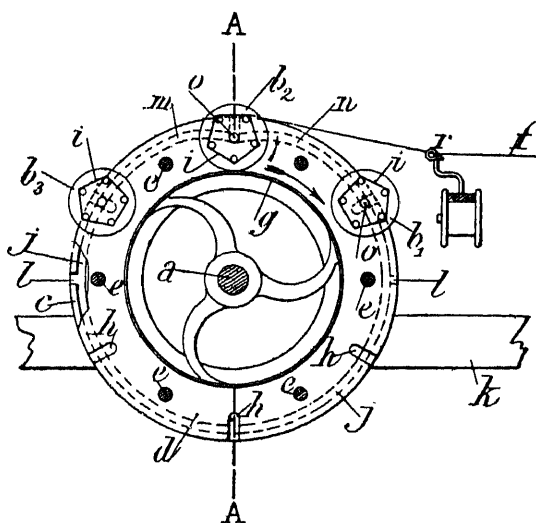


FIG. 142.—The Lumière Spinning Mechanism.

When the spool is full the framework revolves and takes the full spool out of gear and puts an empty one in its place. The periphery of the winding spools is covered with a wrapping of collodion, so that the thread impregnated with the solvent affixes itself tenaciously to the spool as soon as it touches it.

In 1906<sup>1</sup> E. Mertz patented his machine for spinning artificial

under a pressure produced on the hydraulic principle, has a disadvantage that the colloidal becomes clotted and precipitates out when traces of the water leak between the piston and the cylinder wall. In order to overcome this, Lumière (F.P. 361323, 1905) replaces water as the hydraulic medium by a solvent of pyroxylin (preferably amyl acetate), which is pumped into the cylinder and accumulator in the same manner as water in the ordinary press.

1. F.P. 219538, 1892; 364912, 1906; Sw.P. 4449, 1892; for process of "lustering" natural silk see B. Loewe, F.P. 403242, 403243, 1908; E.P. 18086, 18087, 1909; *abst.* J.S.C.I., 1909, **28**, 1310. See also Bâle, F.P. 364912, 1905.

silk, which has been used quite successfully in France and elsewhere, and in which the pipe which supplies the silk solution under pressure is surrounded by another pipe in which a refrigerating liquid circulates. In one form of apparatus the spinning machine consists of a hollow comb-shaped vessel, which is connected to the supply of solution by a pipe and tap. The tooth portion consists of a number of glass tubes with capillary openings. The spinning apparatus is placed in tanks containing an acid solution in order to give the thread a certain consistence, and these tanks are themselves placed in cooling tanks. The threads from the required number of spinnerets are led through a guide, which, by means of an elliptical arrangement of wheels, is made to move to and fro in front of a revolving bobbin, so as to wind the thread into the shape of a bobbin with conical ends. The winding rollers dip into a suitable washing liquid. Another form of spinning apparatus consists of a tube in the shape of a truncated cone. In this is placed a spindle of the same shape which has several fine longitudinal grooves on it. This spindle is pressed into the truncated portion of the other tube by means of a rubber pad. The solution enters at the lower part, and is forced through the grooves on the spindle, which forms capillary openings when the spindle is forced into the outer tube. In another form each capillary opening is furnished with a tap so that any desired number of threads can be spun together. By means of conical driving pulleys the speed of the machine can be altered, and so the fineness of the fibers obtained may be varied.

In W. Crombie's method<sup>1</sup> the cellulose solution is delivered from a perforated nozzle into a vessel through which the coagulating liquid flows without intermission, the level of the liquid in the vessel being kept constant. The outlet pipe, which is immediately below the spinning nozzle, gradually tapers and bends upwards, the effect being that the rate of flow of the coagulating liquid increases and the threads are carried to the end of the pipe without coming into contact with,

1. E.P. 16557, 1908; F.P. 405782, 1909; abst. J.S.C.I., 1909, 28, 978; 1910, 29, 17, Crombie (Fig. 143), relates to apparatus of the kind wherein the solution from which the fiber is to be prepared is successively treated with two different coagulants, and the fibers produced stretched or drawn to a finer size. The solution, supplied through the pipe, B, provided with a rose, comes into contact with the first coagulant in the vessel, A, and the fibers, F, are drawn or stretched during their passage through this vessel. The fibers issue at G into a second coagulant; the latter is supplied from an open trough, H, through an annular inlet, I, the rate of flow being adjusted by raising or lowering the tube, K, through the gland, L. The vessel, A, is filled with the first coagulant by exhausting the air through N. The rate of flow from E is adjusted, so as to keep the liquid in A at proper working strength, and at the same time prevent the second solution in H from rising into A. See W. Crombie and F. Schubert, E.P. 24922, 1908; F. P. 409387, 1909.

and being damaged by the walls. Upon leaving the pipe the threads pass to grooved rollers, or inclined planes, for further treatment.

In order to increase the uniformity of size and structure (denier) of the filament<sup>1</sup> the collodion solution is forced under pressure through the usual capillary openings and then falls vertically through a tube open at both ends and lined with an absorbent material which is kept moist with alcohol so that the air in the tube is kept saturated with alcohol vapor. The collodion thread during its passage through this tube

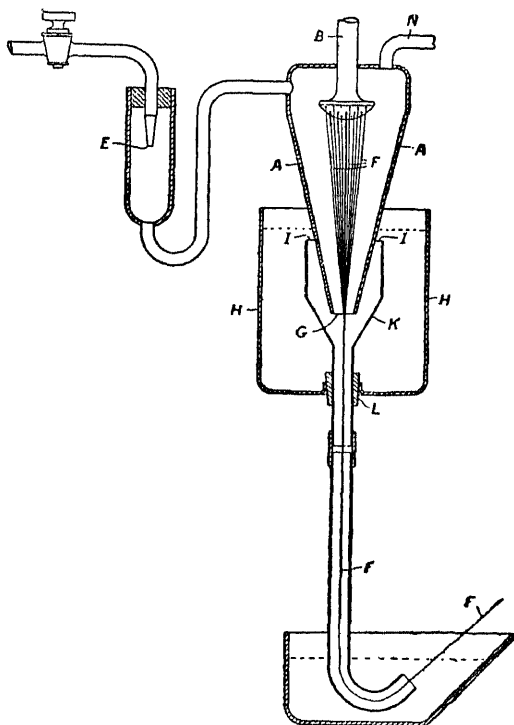


FIG. 143.—Method of Hardening Artificial Filaments According to Crombie.

cannot dry and remains perfectly cylindrical. It then falls into the receiver, which consists of a cylindrical vessel which can be revolved on its vertical axis and contains an inner sieve-like vessel which revolves with it. The receiver is filled with the coagulating liquid. The thread falls into the revolving sieve and is immediately coagulated and arranged in the shape of a truncated cone by the revolution of the receiver. When this sieve is full, it is removed from the receiver

1. A. Lumière et Fils, F.P. 382718, 1906.

and replaced by an empty one. The sieve full of thread is immersed first in water to remove the solvent and then in the denitrating solution.

In the method of E. Ker patented in 1906,<sup>1</sup> the bobbins of artificial silk fibers, after being removed from the spinning machine, are placed in a horizontal position in washing baths, the liquid in which reaches up to the axis of the bobbin. The latter are slowly rotated on their axis in the liquid. The action of centrifugal force is avoided by the slowness of the rotation, so that the liquid is absorbed by the fiber, and penetrates to the lower layers. To dry the latter, they are placed in a drying chamber, and a similar slow rotary motion is given to them.

In another method<sup>2</sup> the filaments immediately after their formation are wound crosswise on bobbins which have an undulating surface, such that an end elevation of a bobbin would have a circumference like that of a cog-wheel. It is claimed that the use of such a bobbin protects the wound filaments from excessive tension and also allows an easy access of liquid to the filaments during subsequent operations.

According to the process of G. Guadagni<sup>3</sup> the filtered cellulose solution flows from a reservoir into a horizontal pipe, supplied on its upper side with short vertical branch pipes at intervals of 15–20 cm. Each of these short pipes is provided with a cock, and terminates in a glass nozzle. Around this glass nozzle is fixed a cylinder, fitted with inlet and outlet pipes, through which the coagulating solution

1. E. Ker, F.P. 366793, 1906; the Soc. Anon. des Celluloses Planchon (F.P. 399218, 1908) describes a spinning machine as an improvement on F.P. 382718, 1906 (J.S.C.I., 1908, 27, 221), being intended to increase the productive capacity of the machine therein described, and to regulate the formation of a fiber of collodion issuing from a nozzle into a vessel containing a liquid by which the solution of collodion is coagulated. The apparatus consists of a number of units, each complete in itself and each containing a nozzle and a vessel to receive the fiber ejected from that nozzle. The nozzles are fed by cylindrical vessels containing collodion and fitted with pistons which are operated by compressed air. By altering the air pressure the supply of collodion to the nozzles is regulated. Each cylinder supplies one or more nozzles. The nozzle is connected to the cylinder by a flexible tube provided with a tap and also with a filter. By a mechanical device the tube moves in a conical path, the nozzle describes a circular path in a horizontal plane, and the receptacle underneath the nozzle revolves on a vertical axis in such a way that its radius corresponds to the diameter of the circle described by the nozzle. The fiber is thus deposited in circles passing through the center of the receptacle and touching its inside wall. The fiber solidifies under the action of the liquid in the receptacle (see F.P. 361960, 1905; abstr. J.S.C.I., 1907, 26, 197), and in this way is said to give a product which can be readily taken out and further manipulated without damage.

2. Gocher Oelmühle Gebr. van der Bosch, F.P. 374790, 1907; E.P. 6942, 1906.

3. E.P. 12253, 1908; A. Clark (E.P. 2695, 1887) prevents agglomeration of the matter around the orifice through which the solution is expelled in being made into threads. This is effected in the following way: superheated steam at 200° is brought to bear on the substance as it leaves the orifice, and this extracts the solvents of the viscous matter and carries them away, leaving the thread quite dry, and the latter may then be spun. In other cases ammonia gas at 100° is used for the same purpose.

flows. Upon leaving the nozzle, the thread rises in this cylinder and is led over a stretching roller, which is run at such speed as is suitable to the rate of the flow of the cellulose solution and the fineness of the thread desired. The driving roller is of the same diameter as the stretching roller and runs at the same speed; it is partially immersed in the washing tank and drives the reeling bobbin (which is entirely immersed in the washing liquor), by direct frictional contact.

In order to give greater uniformity to the filaments the solution may be passed under pressure <sup>1</sup> into a cylindrical box, the bottom of which is furnished with a number of openings for the production of the fibers. Surrounding the upper part of this box is another receptacle in connection with the supply of precipitating liquid, and furnished with a number of fine openings above the level of the capillaries by which the filaments are formed. The whole arrangement is placed at the top of a vertical cylinder, of a length corresponding to the time required for the fiber to set, and filled with the precipitating solution to just above the level of the openings from which the filaments issue. The filaments pass downward through this cylinder in contact with a descending current of precipitant, and pass out at the bottom of the cylinder onto suitable bobbins. This arrangement is stated to give uniform filaments owing to there being no irregular movements of the precipitant. Or the spinning solution may be forced <sup>2</sup> from a reservoir through a number of fine spinning nozzles into a trough, through which flows a steady stream of the coagulating reagent. The newly formed filaments are carried along by this stream and delivered onto the surface of a rotating drum, which is so arranged that the coagulating reagent falls onto it after flowing through the trough. In addition to carrying forward the continuous filaments, the drum is caused in this way to gather up any broken threads. The apparatus is provided with devices for regulating or stopping the flow through each spinning nozzle. In the inventions of H. Tetley and J. Clayton <sup>3</sup> the hollow spindle, which is rapidly rotated, is carried on a swinging frame so that when the nozzle is moved into a convenient position for inspection, the wheels which rotate the spindle are thrown out of gear. A pump for forcing the fluid through the spinning apparatus is likewise so mounted that it can be disengaged from the driving gear at will. The solution passes from a supply pipe to the pump, is then forced through a filter carried by the frame on which the spindle is mounted, and afterwards travels through the

1. As Gocher Oelmühle Gebr. van der Bosch, F.P. 373887, 1907.

2. T. Chandelon, F.P. 394009, 1908; see R. Haddan, E.P. 12879, 1899.

3. E.P. 19157, 19158, 1908.



rotating spindle to the nozzle, which is immersed in a coagulating bath. The thread, which is twisted by the rotation of the spindle and nozzle, is led over suitable guides to a winding reel which is provided with means for laying the thread as it is wound. This winding reel can also be put out of gear and replaced by another reel when required. All the driving means of the apparatus are geared so that they have the required relative speeds, which can be altered at will by a change of wheels. In the second of the present patents (No. 19158) claim is not made for a rotatable nozzle. In the method of the Soc. Boullier and Lafais<sup>1</sup> in order to insure that the spinning of the filament is carried out at the proper temperature, a radiator consisting of a number of steam pipes is arranged behind the spinning frame and adjusted so as to produce around the newly spun filaments the temperature which has been found to be most suitable. The brilliancy of the thread<sup>2</sup> may be increased by adding fatty sulphonic acids to the solvent before spinning.

In the filament-forming apparatus of M. Waddell<sup>3</sup> shown in Figs. 144-146, the spinneret is a combination of two concentric delivery tubes, which are both rotatable about the same axis. The cellulose solution is forced through the outer delivery tube, while the corresponding coagulating solution is forced through the inner tube. The nozzle of the spinning-tube is immersed in a liquid in order to exclude air, and as soon as it is tilted up so that the ends of the delivery tubes are no longer covered, the spinneret is automatically thrown out of gear. The machine is also provided with a filtering device.<sup>4,5</sup>

1. F.P. 392442, 1908; E.P. 15015, 1908; abst. J.S.C.I., 1908, 27, 1201.

2. According to Fab. de soie Artif. Tubize, F.P. 361690, 1905; E.P. 2906, 1906; it is claimed that the oils enter into combination with the collodion without precipitating the nitrocellulose, thus differing from the resins, and being insoluble in water and not completely volatile they leave by evaporation a pellicle on the fiber or product obtained, which increases its stability and resistance to washing.

3. U.S.P. 849822, 849870, 1907.

4. In the method of A. Lumière et Fils (F.P. 361329, 1905) for the filtration of collodion for the preparation of artificial silk, a continuous roll of filtering medium is provided outside the press. A portion of the fabric is clamped tightly over the perforated support by means of a screw-head, and the collodion is admitted under pressure from below through a pipe provided with a stop-cock. When the filtering surface has become clogged, the stop-cock is closed, the conduit for filtered collodion is also closed, the screw-head is raised slightly, and a new filtering surface is pulled through from the roll, and is clamped down ready for use. Their acceptable collodion for artificial silk manufacture (F.P. 361324, 1905) is prepared by dissolving 300 parts of nitrocellulose in 200 parts of methyl alcohol, 200 parts of ethyl alcohol, and 1600 parts of ether. Owing to the excess of ether this collodion is very fluid, and can be easily filtered under a slight pressure. The collodion is then distilled in a vessel provided with stirrers, until 1000 parts of ether have been driven off and condensed for future use. The concentrated collodion is cooled, and, having already been filtered and freed from air while in the dilute condition, it can be directly stored in closed vessels ready for spinning.

5. In forming solid products, such as artificial silk or horsehair, from solutions of cellulose in aqueous solvents, according to the process of L. Cuntz (F.P. 383411,

In U.S.P. 849870, 1907, the end of the spinneret is immersed in a spinning trough containing the coagulating solution. The filaments thus formed travel horizontally along the trough and are taken up by one of two independently removable winding-spools, which are mounted upon a common shaft. In order that the filaments may be thoroughly coagulated, this shaft is so arranged that the spools are partially immersed in the coagulating solution. The trough is provided with a guiding device to deliver the filaments to either of the spools. In the production of threads from a solution of collodion in acetone, the evaporation of the solvent produces a certain degree of cooling of the surrounding atmosphere, and the surface of the

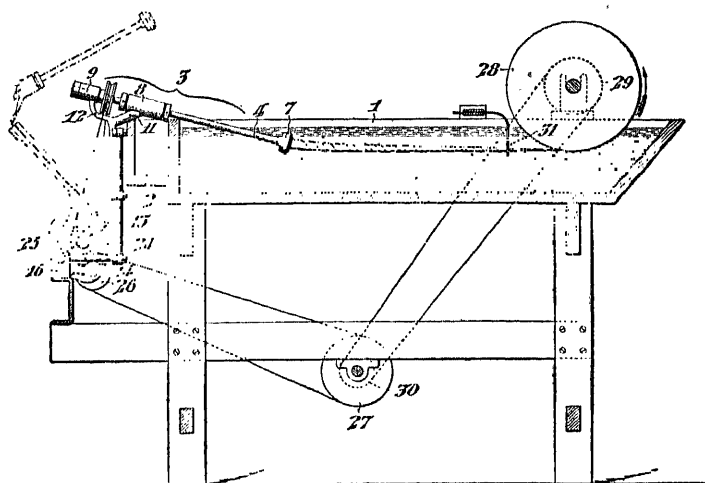


FIG. 144.—The Waddell Apparatus for Forming Filaments.

thread often becomes dull and "milky" from the deposition of moisture. According to A. Cordonnier-Wibaux<sup>1</sup> this may be avoided by passing the newly formed thread in close proximity to suitably arranged sources of heat. The dehydration of fibers produced by the cuprammonium process may be carried out by the same arrangement, and the strength of the fibers is improved. J. Boullier<sup>2</sup> has found

1907), the cellulose solution is first caused to pass from the delivery orifices through a medium in which it may be moulded to the desired shape but not coagulated, and thence directly into a bath which rapidly solidifies the moulded cellulose. The moulding medium may be either gaseous, e.g., the air, or a liquid, such as acetone, benzene, petroleum, carbon bisulphide, oil, turpentine, etc. This moulding liquid may be contained in the same vessel as the coagulating liquid, on which it floats as a superficial layer.

1. F.P. 401343, 1908.

2. F.P. 368190, 1906; E.P. 16512, 1907; abst. J.S.C.I., 1906, 25, 1217.

that this milky appearance is due to the solvents employed having too low a vapor tension, and can be overcome in the following ways:

- (1) By seeing that the solvents are quite free from moisture.
- (2) Addition of a body like ether.

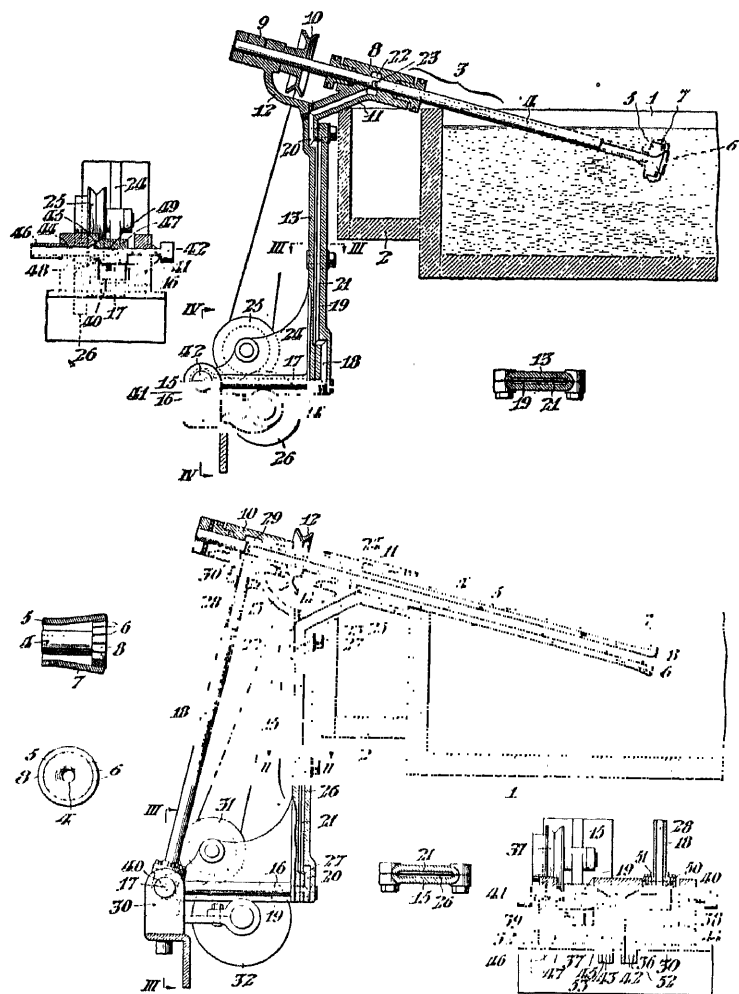


FIG. 145.—The Waddell Apparatus for Forming Filaments.

(3) By spinning the filaments in a temperature so high as to increase the vapor tension of the solvent employed.

In the method of C. Bouillot<sup>1</sup> the filaments, on issuing from the

1. F.P. 373947, 1906; see also J. Douge, U.S.P. 699155, 1902; E.P. 2476, 1902.

capillary tubes, are received on a polished heated cylinder made of glass or metal, and revolving at a speed corresponding with the rate of production of the fiber. From this cylinder the filaments pass, a certain number at a time, through a forked guide which moves transversely across the surface of a revolving bobbin and so winds the compound thread in a spiral manner. This bobbin rests on another cylinder which revolves at a similar lineal velocity to the drying cylinder and drives the bobbin by friction. The whole apparatus is inclosed in a metal box from which the evolved vapor can be removed by aspiration. The box is provided with a glazed opening through which the operation can be watched and which also serves for the removal of the bobbins when these are full.

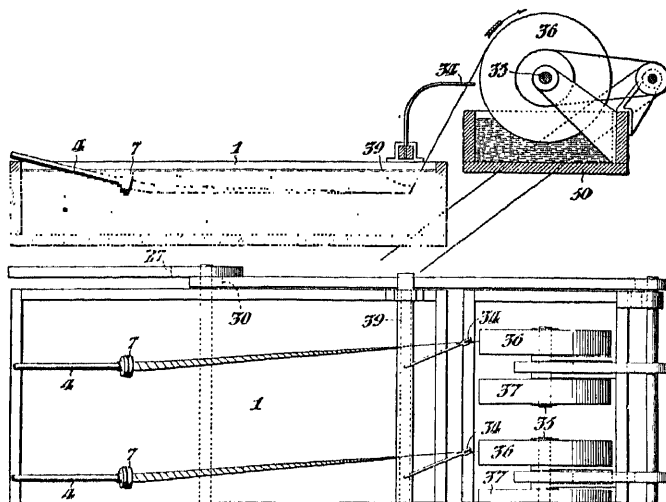


FIG. 146.—The Waddell Apparatus for Forming Filaments.

For some time it has been known that nitrocellulose containing a certain amount of water was more soluble in a mixture of alcohol and ether than a dry nitrocellulose, and from this observation has been evolved several methods of introducing a definite quantity of water into the nitrocellulose solution, before the latter is forced into filamental form. Thus F.P. 231230, 1893, recommends the use of a nitrocellulose containing 25-30% of water. G. Dietl<sup>1</sup> has secured a patent, the object of which is to produce a thread that will dry immediately on exposure to the air, and which will not stick together. In producing a very thick thread it is necessary to twist several thin threads together, and it has been found that a nitrocellulose contain-

1. F.P. 356323, 1905; E.P. 15029, 1905.

ing 33-38% of water is most suitable, 30% of water being insufficient. With this amount the nitrocellulose can be dissolved in the proportion of 17-23 k. in 100 l. of the usual solvents, and will then spin a thread which does not stick. J. Stoerk<sup>1</sup> obtains best results with a pyroxylin containing 12-20% water, while the method of B. Julich<sup>2</sup> is characterized by the fact that pyroxylin containing 21-24% of water gives best results. G. Lacroix<sup>3</sup> claims to be able to spin satisfactory filaments with a nitrocellulose containing 35-45% water, the solvent preferred being equal parts of alcohol and ether. It is important to use relatively mobile solutions rich in nitrocellulose, in order to be able to force the solution through fine openings with the smallest possible pressure and to obtain uniform filaments. E. Berl<sup>4</sup> states that highly concentrated solutions of nitrocellulose, of relatively low viscosity, can be prepared if the dried cellulose before nitration be heated to a high temperature for a long time in presence of inert gases free from oxygen (carbon dioxide, nitrogen, water gas, cooled fire gases, superheated steam). Under these circumstances the cellulose is depolymerized to a degree varying with the temperature and duration of heating. It is stated that with cellulose treated in this manner the cost of manufacture of smokeless powder is lessened, owing to the increased yield of nitrated product, the possibility of repeated regeneration of the nitrating mixture, and smaller consumption of solvents.

In the so-called Topham turbine system of collecting and spinning the threads at the same time,<sup>5</sup> which has been previously used in the spinning of short-fibered yarns, principally asbestos, the squirted thread passes over a roller and thence into a rapidly rotating box. As they are fed in, the fibers are twisted together, the centrifugal force causing them to form a compact coil around the interior of the box and to be formed into hanks or skeins. If the boxes are deep, a longitudinal reciprocating movement can be given to either the box or the funnel to make sure of the even coiling of the thread in the skein form. It is said to reduce to a minimum the strain on the newly formed threads.

In spinning machines for producing artificial fibrous material, such as described, for instance, in certain<sup>6</sup> earlier patents of R. Strehlenert, and in which the spinning or twisting takes place by force of gravity and the current of coagulating liquid is made use of for taking

1. E.P. 26982, 1902.

2. E.P. 27527, 1906; F.P. 371544, 1906.

3. E.P. 2192, 1905; F.P. 351265, 1905.

4. D.R.P. 199885, 1907.

5. E.P. 23158, 1900.

6. U.S.P. 702163, 1902; D.R.P. 96208, 101844, 102573, 1897; E.P. 3832, 1897; 58, 1899; Sw.P. 13695; see also "Die Künstliche Seide," C. Suvern, 1900, p. 60.

up the torn fibers, the apparatus can only be set to work either at starting or after an interruption—for instance, in consequence of the rupture of all fibers fed by the press, when the fibers are caught hold of by hand—i.e., the textile fibers leaving the openings must be dipped down to the bottom of the spinning-cone for the coagulating liquid by means of a piece of wire and caught hold of by means of a second wire introduced into the collecting-tube and drawn up to a spool on which the thread is wound. Since this operation is very tiresome and the quick collecting of the pressed-out fibers requires great practice in order not to lose too great a quantity of the dissolved spinning material, R. Strehlenert<sup>1</sup> has improved on his older processes noted above and has perfected an invention which has for its object an automatic collection of the fibers at the starting of spinning, as well as after a complete or partial interruption of the operation. The collection of the torn fibers and the further leading on of the bundle of fibers coming from the spinning-cone are permitted by the arrangement of a return-conduct which is designed to lead the coagulating liquid between the spinning-cone and the collecting-tube arranged as a prolongation of the same to the spinning-cone. By allowing the return-conduct to enter the inside of the spinning-tube tangentially a rotation of the liquid is attained.

On the accompanying drawings (Fig. 1-17), 1 and 2 show the apparatus in longitudinal section and in plan.

The pressing-nozzle *A* is arranged in the spinning-cone *B*, which is destined for holding the coagulating liquid and which ends into the collecting-tube *C* for the spinning material or fibers *H*. The upper end of this tube *C* and the spinning-cone *B* are connected by a communicating-tube *D*. The bundle of fibers leaving the nozzle causes, by adhesion of the liquid on the fibers, a current, which sets up a circulation by aid of the return-conduct. The tube *D*, which is intended to lead the coagulating liquid into the cone *B*, is preferably positioned tangentially to the periphery of the cone *B*. The coagulating liquid is introduced into the tube *D* by an elbow-pipe *E*, fixed to the tube and directed toward the cone *B*. By this arrangement the advantage is arrived at that in the cone *B* the current of liquid is greater and quicker, since the stream of liquid passing out from the pipe *E* carries with it fluid from the upper and widened part of the tube *C* and acts

1. U.S.P. 716138, 1902; E.P. 28361, 1902; in order to decrease the tendency of the filament to absorb water and swell up, thus reducing its strength in the wet condition, Strehlenert (E.P. 22540, 1896; Mon. Text. Ind., 1897, 12, 752) mixes with the nitrocellulose solvent before drawing out the threads, formaldehyde, acetaldehyde, paraldehyde, benzaldehyde or other aldehydes, in amounts up to 15% of the weight of the nitrocellulose. See also Strehlenert and F. Reubold, U.S.P. 812098, 1906.

like an ejector, thereby rotating the liquid in the cone *B*, which at the same time has a continually increasing velocity by reason of the funnel shape of this portion of the moving body of liquid. According to this arrangement it is not required to introduce a greater amount of new liquid than is necessary for the coagulation of the fibers. However, the effect of the amount of liquid serving to collect the torn fibers is in this case so great that this quantity is able to collect complete bundles of fibers, when the apparatus is set to operate from the beginning, or after an interruption of the operation has taken place.

In order to prevent the bundle of fibers from slipping back with the current into the tube *D*, the mouth *F* of the same is covered, for instance, by a fine-wire net or the like. (Not shown.) Any superfluous coagulating liquid runs off through the overflow *G*.

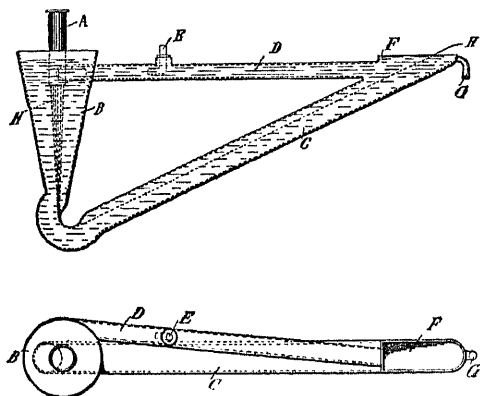


FIG. 147.—The Strehlenert Method of Spinning and Twisting Artificial Fibrous Material.

The processes of X. Eschaliér<sup>1</sup> particularly adapted for the treatment of artificial silk products for the purpose of "sthenosage" (strengthening the threads), consists in the action of aldehydes, especially formaldehyde, upon cellulose and albuminoid bodies in the presence of acids or acid salts in conjunction with dehydrating agents. Artificial silk, for example, is placed in a bath of formaldehyde (1–10 parts) and acetic acid, 10–40% (90–99 parts). The threads after removal from the bath are placed in a desiccator containing calcium chloride or sulphuric acid until completely dry, and are afterward heated for four to five hours at 40°. Finally, they are washed in

1. E.P. 25647, 1906; F.P. 374724, 1906; First Addition thereto, dated Nov. 5, 1906; Second and Third Additions, dated Oct. 7, 1908; Fourth Addition, dated Mar. 31, 1909; abst. J.S.C.I., 1907, 26, 821, 1292; 1908, 27, 157; 1909, 28, 362, 1121.

water and again dried. Another method consists in placing the threads in a bath of glacial acetic acid containing formaldehyde for three to four hours at 90–95°, and afterward washing with water and drying. The aldehyde and the dehydrating agent which are employed for strengthening artificial silk may be applied to the material either alternately or simultaneously. The following process gives good results. The material to be treated is impregnated with a solution of lactic acid and alum of such a concentration that the fiber retains 5–6% of its weight of each reagent. It is then placed in a closed vessel containing a dehydrating agent such as sulphuric acid at 50–60°. Through an opening in the wall of the vessel 10–25 parts of a 40% solution of formaldehyde are introduced for each 100 parts of material. The opening is then sealed and the apparatus heated to 50–60° for a further five or six hours. The material is then removed, washed, and dried. Fibers which have been treated in the manner described in this patent exhibit an increased affinity for dyestuffs if treated with a solution of sodium or potassium hydroxide. If a concentrated solution be employed, the time of action must be short or the strength of the fiber will be affected and its length diminished. Oxidizing agents such as hypochlorites may be added to the solution. The reagents used for the "sthenosage" may be dissolved in other media than water, e.g. acetone, alcohol, glycerol, etc. The use of acetone is particularly advantageous, since it dispenses with the usual process of dehydration. The dry silk is introduced into a bath composed of 150–200 parts of acetone, 5–20 parts of 40% formaldehyde and 0.5–0.15 parts of sulphuric acid of 66° Bé. or hydrochloric acid of 23° Bé. These quantities are sufficient for treating 10 parts of silk. The whole is boiled for three to five hours under a reflux condenser, the silk being completely immersed. The silk is then washed with water and dried. When required for dyeing, the silk is subsequently steeped in an alkaline solution of a hypochlorite, containing 30–50 gm. of sodium hydroxide and 3–5 l. of available chlorine per liter. Other acids may be used, if desired, instead of the mineral acids.<sup>1</sup> The effect of this treatment on the physical prop-

1. An ingenious process has been worked out by W. Morton (U.S.P. 705691, 1902) for the formation of artificial silk filaments, which in its broad scope relates to the electrical method of dispersing fluids, whereby volatile fluids are separated from their combination or association with relatively non-volatile or fixed substances in composite fluids, resulting also in the evaporation of the volatile fluids and a state of condensation or solidification of the relatively non-volatile or fixed substances, whereby fiber may be artificially produced. Broadly speaking, the process is practiced by delivering the composite fluid in an attenuated form into an electrically polarized atmospheric field produced by the convective passage through an atmospheric medium of an electric current of high tension. According to the inventor, if a quantity of a composite fluid to be thus electrically dispersed and separated be delivered in a fine stream or streams or finely divided state into



erties of the lustra celluloses, as recalculated into mean or average numbers by Cross and Bevan<sup>1</sup> is as follows:

	Breaking strain gms. per unit denier.		Elasticity elongation per cent.	
	Air dry conditions	Wetted.	Air dry.	Wetted.
For the lustra celluloses of the three processes, nitrocellulose, cuproammonium, viscose .....	1.25	0.37	12.2	9.0
Sthénose products .....	1.6	1.1	7.8	7.6

These results have been independently verified.

a polarized atmospheric field or path of a convective discharge between the polar terminals of an active source of electricity of high tension, a separation of the volatile component from the fixed component occurs and contemporaneously the fixed component is broken up or disrupted, the volatile component is evaporated, and simultaneously the fixed component is condensed or solidified. If a viscous solution of a tenacious fixed substance capable of setting or hardening while in a filamentous state is delivered in the manner above mentioned to the convective discharge, the volatile component is separated from the fixed component, and coincident therewith the rapidly condensing fixed component is broken up or disrupted into filaments by the action of the convective discharge, which are rapidly dried and solidified in a fibrous condition adapted to be used for textile or other purposes, according to the nature of the fixed component. It is preferable when employing heavy viscous composite fluids that the fluid upon which the process is to be practiced should be projected or delivered into the path or field of the convective discharge in an attenuated or finely divided form. If the composite fluid is viscous and its non-volatile component is capable of setting or hardening upon being deprived of its solvent, such as collodion, and the electrical tension is properly graduated to the delivery of the fluid, then fine long filaments are produced by the electrical disruption of the fluid after delivery into the convective field, and the filaments of pyroxylin will dry or set very quickly on account of the quick separation or evaporation of the volatile component, and the electrical dispersion of these solutions usually produces multiple threads or fibers of the fixed component, and these threads or fibers set or harden and dry with great rapidity. If the stream of the fluid discharged into the electrical field is continuous, the process of disruption of the fluid is also continuous, provided the electrical convective discharge is continuous, and hence by providing a continuous delivery of fluid into the path of a continuous electrical convective discharge the operation of the production of these fibers is continuous and the fibers may be collected mechanically—as, for instance, by reeling—as fast as they are produced. For the production of a field of convective discharge is employed any suitable source of high-tension or static electricity, such as a Holtz static machine, induction coils of large size, or the Tesla, Thomson, and other machines now well known for producing currents at enormously high voltage. Many different varieties of composite fluids the fixed component of which is sufficiently tenacious and adhesive for the purpose possess the property of being converted into fiber under the effect of high-potential electrical discharges. Among the materials for the making of fiber in this way being collodion, so-called "flexible" collodion (ordinary collodion to which has been added 5% Canada turpentine and 3% castor oil), and a solution of pure rubber and sulphuric ether.

This is similar to the process of Soc. Anon. "Le Crinoid" (U.P. 410827, 1909) who add formaldehyde to the solutions of sodium hydroxide or carbonate used to coagulate cuprammonium cellulose solutions, to produce a more powerful coagulation, to form stronger threads, and to facilitate the recovery of copper from the spent baths. The most suitable additions for concentrated alkaline baths, to be used at 30–45°, are from 1.5 to 5% of 40% formaldehyde.

1. J.S.C.I., 1908, 27, 1189. They say "In regard to the proportion of methylene

In the apparatus of E. Friedrich,<sup>1</sup> as shown in Fig. 148, the essential characteristics are that the twisting together of the separate threads does not occur until each separate thread is coagulated and hardened, so that the gumming together of the threads is obviated. The cellulose solution from which the threads are to be produced issues from the tube *a* through a number of fine apertures in the nozzle *b* into the tube *c*, to which at the same time the coagulating liquid is supplied through the pipe *d*. The threads issuing from the nozzle *b* are coagulated or hardened by the coagulating liquid as it passes with them in upward direction in the tube *c* parallel to its axis.

The threads are twisted together on entering with the coagulating liquid into the interiorly grooved portion *e* of the tube *c*, which, owing to its interior helical groove, imparts a rotatory movement to the liquid. In case one of the threads is ruptured by the rotation imparted to them by the liquid the broken portion is immediately twisted again onto the main thread. The threads can be twisted around each other as frequently as desired by the properly selected number of turns or windings in the helical groove portion in the tube *c*. This cannot be accomplished in apparatus in which the entire body of the liquid is rotated.

The finished thread issues from the upper part of the apparatus at *f*, while the coagulating liquid is drawn off through the pipe *g*. The thread is wound upon the roller *h* or conducted away by it. To obviate the necessity of unwinding<sup>2</sup> certain kinds of silk after precipitation, an arrangement is proposed in order to rewind it into skein form, by which the thread is skeined without any intermediate reeling. The thread passes round an ordinary reel, which draws it

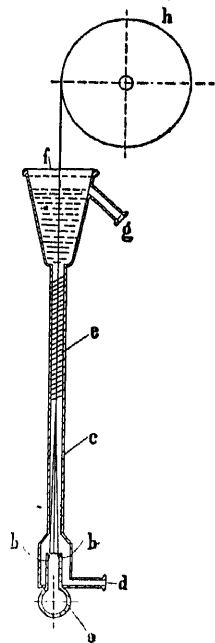


Fig. 148. The Friedrich Spinning Apparatus.

oxide fixed in combination, our own analyses of Sthénose silk, have given numbers between 0.35% and 0.8% formaldehyde, which expressed in molecular ratio,  $C_6H_5O:C_6H_{10}O_5$ , is approximately 1:30. This indicates a curiously disproportionate effect. It might be assumed in explanation that the fractional proportion of molecules or groups actually reacting are in the free or uncombined state capable of influencing the hydration capacity of the complex or aggregate, or as an alternative the suggestion is that a constitutional change in the cellulose itself accompanies the fixation of the  $C_6H_5O$  groups, and this suggestion is of moment, as it indicates a capacity of internal structural modification which offers an attractive field for research."

1. U.S.P. 827434, 1906.

2. Method of La Soc. Anon. Fabr. de Soie Artif. de Tubize, E.P. 3025, 1906.

through the precipitating liquor, and passes direct to a calibrating reel, upon which it is skeined. This reel is provided with a revolution counter, and the tension of the thread is kept constant by a counterweighted brake upon the ordinary (intermediate) reel. Should the thread break, the calibrating reel is brought to a standstill automatically. In order to increase the evenness of the artificial threads<sup>1</sup> they are cross-wound upon longitudinally corrugated reels immediately after their formation.

**Comparison of Yarn Sizes.** The bulk of the artificial silk at present produced is spun in 150–160 denier<sup>2</sup> sizes, equivalent to 37s to 40s cotton yarn. The 120 denier thread of to-day<sup>3</sup> varies in the number of the individual filaments, but it may be said not to exceed 25 in number, so that the size of the individual filament may be taken as from 5–8 denier. Real silk averages 2.75 denier per filament. The fine Cellulo silk (30–50 denier) may contain 45–60 filaments, which would make the size from 0.5–1.2 denier. Dreaper has also described artificial filaments of a tenuity as great as 0.33 denier—about one-eighth the size of a filament of natural silk. The present demand, however, is confined to the ordinary range of 100–130 deniers, although the lower deniers down to a 15 denier thread is no doubt a near commercial

1. Process of O. Müller, E.P. 3606, 4015, 1907.

2. The relative fineness of artificial silks is classified according to the international denier, a "denier" representing the weight in milligrams of a filament 10 meters long. It applies equally to the single filament (brin) or to the combination of these—usually 10–25—which constitutes the weaving unit. Thrown silk in the United States and England is usually based on the weight in drams of 1,000 yards. In France the size of silk is usually expressed in terms of the old denier, which is the weight in deniers of 400 ells, equivalent in length to 476 meters, the denier weighing 0.05313 gm. Old system deniers are convertible into international deniers by multiplying by 1.116, and conversely, by multiplying by 0.896. According to Cross and Bevan, "Researches on Cellulose," 22:

"In speaking of a yarn of 80 deniers having a 'tenacity' of 96 gm. and an 'elasticity' of 12, we are shortly expressing the ultimate facts as follows:

"The yarn weighs 0.080 gm. per 10 meter length, and breaks when stretched with a weight of 96 gm., having undergone an elongation of 12% in length. Assuming 16 unit filaments in the yarn, each is of 5 deniers and would bear one-sixteenth of the stretching weight. Taking an average diameter of the unit at 0.03 mm., this implies a sectional area of 0.000707 mm. square; and the tenacity may therefore be expressed as being equal to

$$\frac{6}{0.000707} = 8,486 \text{ gm. per mm. square,}$$

which at once conveys the relationship of cellulose to other structural materials which are capable of being produced as a regular solid in continuous length, e.g., the metals.

"Another form of expression which has advantages in comparing structural quality is the *breaking* ' ' ' ' length of the material which, supposed extended in space, will ' ' ' ' in the above case

$$\frac{96,000 \times 10}{80} = 12,000 \text{ meters.}''$$

3. W. Dreaper, J.S.C.I., 1909, 28, 1297.

probability. It must be borne in mind, however, that a large proportion of artificial silk is used as the warp in textiles where the weft is real silk and that the finer the denier the greater covering power per unit weight. And as the value of these textiles depends not upon the weight, but upon the covering power and hence the appearance, it is evident that in considering the latter the finer deniers are desirable.

**Dyeing of Artificial Fibers** comprises not only the artificial silks, but artificial horsehair, straw plaits, mixtures of non-lustrous curly waste from artificial silk manufacture with wool or shoddy, and similar waste, carded and spun by itself. Artificial fibers may be dyed either by direct coloring while preparing the solution for projection through the minute orifices in the formation of the silk filament, or by dyeing the finished skeins. The first-named procedure has the appearance of being the more simple and suitable one, but practical experience has shown that the better way is to dye the fibers after formation into skeins. Dyeing the artificial silk while in course of formation consists in simply dissolving the appropriate dyestuff in methylated spirits or denatured ethyl alcohol, and adding to the filtered collodion a filtered solution of this dyestuff.<sup>1</sup> It is necessary to color the collodion very intensely that a heavy depth of shade may be produced in the final filaments, and the dyestuff used must be very carefully filtered from any undissolved particles, in order to guard against stoppage of the minute orifices through which the solution is projected in the formation of the filament. Another drawback to this method is that with colored solutions the contents of at least an entire cylinder must of necessity be dyed of the same color, whereas where the dyeing is done in the hank form, amounts of various colors may be dyed at the option of the manipulator, and the depth of shade can be governed closely. For these reasons, the production of dyed silk in this manner from collodion solutions has been almost entirely abandoned. Denitrated collodions have a much stronger affinity for basic dyestuffs than Glanzstoff or viscose silks, and full shades can be dyed direct on the former, whereas the latter must be mordanted, usually with tannin. Substantive colors go on artificial silk too easily

1. E. Jentsch (Färber-Ztg., 1908, 19, 36) notes that Chardonnet silk is peculiar in that it takes up basic colors without the aid of a mordant; the substantive cotton colors are best absorbed by "Glanzstoff." Chardonnet silk, however, gives fuller and faster dyeings with basic colors when previously mordanted with tannic acid and tartar emetic. Details of the methods of dyeing artificial silk and of the colors most suitable for the purpose are given. It is stated that dyeings with the substantive cotton colors are often "topped" with basic colors in order to brighten them. Shades which appear dull on drying are often brightened by steaming for a short time. In dyeing both Chardonnet silk and "Glanzstoff," the temperature of the bath should not exceed 70°, a lukewarm bath being used at the commencement of the operation. The dyeing usually takes from one to two hours.

and quickly for level dyeing, unless the dyestuff be considerably diluted. Chardonnet silk is peculiar in that it takes up basic colors to full shades without previous mordanting, whereas the substantive colors are best absorbed by Glanzstoff. These observations are explained by the fact that Chardonnet silk is made from nitrated cellulose and therefore probably contains oxycellulose, while Glanzstoff is merely a different form of cotton cellulose. Chardonnet silk, however, gives fuller and faster dyeings with basic colors when previously mordanted with tannin and tartar emetic, the fastness of the shades being better than on mercerized cotton (near-silk or luster). It has been found that where the dye-bath is too hot there is a diminution in luster, while the threads soften and stretch unevenly. It therefore should be handled very carefully at all times, especially when wet, and under no circumstances should it be allowed to lie around wet for any great length of time. When it is remembered that there is a diminution in strength of about 60% shown when in the wet state, the reason for careful handling in this condition becomes apparent. Drying, however, restores the strength of the fiber to its original condition, especially if the fiber has been allowed to absorb from the atmosphere its "normal hygroscopic moisture." The temperature of the dye-bath should not exceed 60°, and is better carried out at about 45–50°. Great care should also be exercised in turning the skeins, on account of their tendering in the wetted condition, more apparent with a rise in temperature of the water. Well polished bamboo sticks and rivetless copper kettles are recommended,<sup>1</sup> although the usual wooden dye-box to the author's knowledge is in daily use with apparent satisfaction. Certain dyestuffs go on artificial silk very unevenly, and this lack of uniformity is not always apparent when using the same dyes,<sup>2</sup> often leaving spots entirely or nearly white. This unevenness has been considered<sup>3</sup> as a demonstration of the heterogeneity of artificial fibers

1. According to F. Beltzer, *Mon. Sci.*, Apr., 1907, 237, commenced Feb. 1907, 88,

2. L.c.; according to W. Minajeff (*Z. Färb. Ind.*, 1909, 7, 236) comparisons of the action of dyes on Pauly silk and cotton indicates relative to the latter, that (1) the cuticle of the bleached fiber has no influence on the dyeing process, (2) the lamellar structure of cotton plays no part in differentiating its dyeing action from that of Pauly silk, and (3) the canals in the cotton fiber play no important action, mordants and lakes depositing in the canals to only a very limited extent. The determining factors are thickness, density, and capillarity, rather than microscopic structure.

3. V. Clement (*Färber Zeit.*, 1909, 20, 1) states that all the artificial silks possess the defect, when dyed in bulk or in the cloth, of giving stripes of different intensities of shade. In the collodion silks this defect has been traced to differences in the percentage of residual nitrogen (1.23 to 1.61) remaining after denitration, the darker shades corresponding to the higher percentages of nitrogen. In the case of "Glanzstoff" and viscose silks, the darker stripes correspond with a more pronounced oxycellulose reaction. The author thinks that the differences are not due to any irregularities of the chemical treatments subsequent to the formation

as compared with the homogeneity of natural ones. Topping lightly with basic dyestuffs often remedies this difference, and adds brightness and tone to the shade.<sup>1</sup>

In a general way, dyeing with the various sulphide colors, so advantageous with viscose filaments, proceeds the same as with direct or cotton colors, care being taken to keep the temperature below 60°, and using a smaller amount of dyestuff and Glauber salts.<sup>2</sup> The dye-bath should be prepared, heated to the desired temperature, and the dyeing operation proceeded with as promptly as possible. Proper wetting out of the "silk" is very essential, and this means that the temperature of the water should not be below 48°, nor above 60°, the immersion being only sufficiently long enough to permit of thorough wetting of the fibers. Omission of this point is frequent cause of uneven dyeings. The volume of the dye-bath in relation to the amount of silk to be dyed is an important consideration, 3.5 U.S. gal. to each pound of silk being found best suited for all shades and classes of colors, while in dyeing blacks and certain very heavy shades, as bottle greens, dark blue and intense reds and yellows, the proportion of water to silk may be diminished.

The wetted skeins, either before or after mordanting and depending on the class of dyestuff it is desired to deposit on the fiber, is immersed in the warm dye-bath, turned carefully but continuously until the required shade is obtained, taken out and allowed to drain, but not wrung by hand on account of their tender condition, when after cool-

of the threads, but are caused by uncontrolled changes in the cellulose, taking place under the influence of the alkaline agents employed for dissolving the cellulose prior to spinning. The product of every batch is stated to be uniform as regards its dyeing properties, but is always irregular in count ("denier"). Since this cannot be controlled, the skeins are sorted according to "denier" afterward, and skeins from several batches are parceled together, one batch having a different affinity for dyestuffs from another. Artificial silks must be bleached rapidly; alternate treatments with sodium hypochlorite and hydrochloric acid give the best results; the permanganate bleach weakens the fiber. For dyeing, the basic dyestuffs of the "janus" group give the best results as a rule. On collodion silks the "janus" colors give full shades direct, fast to light and to water; the other silks show equally good results on tannin mordants. The "seto" dyestuffs are also good but not particularly fast. Many of the acid dyestuffs are suitable for the direct dyeing of pale shades, fast to light but not to water. The substantive dyestuffs are used very extensively, but are not suitable for "navy blue"; this color is best obtained by janus blue R or indoin blue toned with methyl violet. For black, janus black gives the finest shades. All dyestuffs are somewhat less fast to light on artificial silk than on cotton. The author concludes with a table of tests for the artificial silks. It is difficult to distinguish between "Glanzstoff" and viscose silks; the latter, however, gives a somewhat darker shade with Schiff's reagent than the former.

1. By reason of the threads swelling greatly they take the dye more rapidly than is the case with natural silk, and for light and delicate shades great care has to be exercised not to over-dye.

2. Overheating during drying should be avoided, and under no circumstances should the silk be left in the dry-room after it has become properly dried.

ing to the room-temperature, the hanks are preferably wrapped in cloths and hydro-extracted in a centrifuge. They are then placed in a drying-room heated to not above 40° for the removal of the remainder of the moisture, and when dried are allowed to cool gradually without being touched and to assume their normal amount of moisture from the air before being removed. This is necessary on account of the fact that when deprived of all moisture the filaments are quite brittle, but regain their elasticity upon absorption of moisture again. In dyeing with the direct colors, and less frequently with the basic colors, standing baths are to be used in the same manner as in cotton hank or piece dyeing, the actual value of the partially exhausted bath depending in a large measure upon the volume of business done by the dyer and whether the run on a particular shade is heavy or frequent enough to warrant keeping up a standing bath. The luster may be increased by drying under tension.

Shades that are found after drying to be too deep may be somewhat lightened by a short and very careful process of steaming, while conversely, shades that are considered too light may be intensified by increasing the temperature of drying, which often has a tendency to darken the shade. Sodium carbonate facilitates the application of the substantive dyestuffs, and Monopol soap or Turkey-red oil favors the production of evenness in dyeing and a soft feel. Washing in cold water should follow dyeing, and then a cold bath containing, for brightening purposes, acetic acid and a trace of soap. A little acetic acid may be added to the dye-bath, but no soap, Turkey-red oil or other softener must be added at this stage, for they form a dull lake with the basic colors.<sup>1</sup> Dry artificial silk is said to absorb 16% of its own weight of moisture as against 11% by natural silk. Arti-

1. E. Mertz (F.P. 364913, 1906) has devised a process for dyeing artificial silk wound on bobbins by machinery. The bobbins carrying the material are supported at each end by bearings fixed to two endless vertical chains. These chains can be revolved intermittently by means of gearing connected with a lever-and-cam arrangement. The edges of the bobbin reels are in contact with a vertical plate faced with caoutchouc, and placed on one side of them. The reels press against this, and are thus caused to revolve on their axes during the upward motion. The liquid to be applied is forced over the uppermost bobbin through a perforated pipe, and is caught in a vessel placed beneath the bobbin. This vessel is also perforated, and the liquid thus falls on to the next lower bobbin, and so on to the bottom. The material is thus submitted to a liquid becoming more and more pure as it rises to the top of the machine. The bobbins are removed at the top, and fresh ones inserted at the lower part of the endless chain.

According to E. Dierichs (D.R.P. 211956, 1907) dyed cotton fibers are woven with undyed artificial silk, and the fabric thus obtained is treated with an alkaline solution, whereby the color is partially discharged from the cotton and is taken up by the artificial silk. An example is given in which two lots of cotton are mordanted with tannin and dyed with methylene blue and brilliant rhoduline red; the fabric made from these and the artificial silk is treated for half to three-quarters of an hour, at 40-50°, with a 1% solution of sodium sulphide.

ficial silk cannot be weighted as the natural silk, due to at least two causes—the fiber will not absorb the metallic oxides, and even if it did, its nature is such that it will not stand the temperature, nor the handling necessary. When the artificial product is “horsed” lightly after drying, it has a luster superior to that of natural silk, and to give it a “scroop” also, it may be passed through a soap bath, and afterward through a dilute solution of acetic, or better, tartaric acid.<sup>1</sup>

There is no one manufacturer's series of dyestuffs markedly superior for artificial silk dyeing. V. Clement<sup>2</sup> especially recommends the

1. The luster of artificial silk, especially where developed to the maximum by tension during drying is somewhat metallic on account of double refraction, seen more conspicuously with the cellulose nitrate silks. This double refraction causes many dyes to fluoresce on artificial silk to such an extent as to preclude their use. The difference between the price of artificial silk and the natural product is in reality not so great as would at first appear, on account of the fact that the first named has a greater specific weight and more transparency than the second. As a consequence, a correspondingly greater amount of artificial silk is required to supply the same covering power given by natural silk. For passementerie, where the silk is employed massed thickly and embedded, this characteristic is of very little importance; indeed, artificial silks are used largely to replace in part or wholly, weighted natural silks. The tensile strength of artificial silk is also lower in the dry state than that of the natural product, and becomes much lower still when damped; dyeing in machines consequently presents some difficulties.

2. L.c., has found that for general purposes the basic dyes are very suitable, and particularly the janus colors of the Hoechst works, the dual character of which in behaving as basic dyes and as the substantive dyes makes them very serviceable; also the seto dyes of the Geigy works, which, when regarded chemically, resemble the acid coloring matters. The first-named supply on collodion silk, without any mordant, colorings that are fairly fast to water; they also give deep shades on the cellulose silks. Setoglauceine and setocyanine of the second class have to be singled out for mention, on account of the facility with which very level dyeings may be obtained, though the colors possess no particular degree of fastness.

Collodion silk may be dyed directly in very deep shades, but the cellulose silks in light and medium shades only. For deep shades on the latter, and also if fastness to washing be demanded, a preliminary mordanting with tannin is necessary. The material, however, should not be steeped overnight in the tannin; as a matter of fact, an immersion extending to one or two hours is quite long enough, this to be followed by squeezing and a passage through a cold bath of tartar emetic. It is useful at times to diminish the affinity of the tannin for the fiber by employing it in a cold solution. A goodly number of acid dyes are available for the dyeing of artificial silks. Foremost are quinoline yellow, victoria yellow, orange 2 and 4, metanil yellow, brilliant orange, brilliant croceine, phloxine, acid rosamine, fast acid violet, soluble blue, patent blue, erioglauceine, erioecyanine, and acid violet. These coloring matters serve for the production of a variety of shades mostly in pale tones, and also for bright red, though these are fast neither to light nor to water. When incompletely denitrated, collodion silk fixes the acid dyes in a fashion to give shades fast to soaping, but not when completely and sufficiently denitrated.

In a general way both collodion silk and the cellulose silks behave similarly toward the acid dyes. The basic dyes, the janus dyes, and the acid colors are each applied in the same manner. The material is first damped in tepid water and entered into the dye-bath acidified with acetic acid or alum; the solution of the coloring matter is then added, and the silk dyed for a quarter of an hour in the cold, and for a further half hour at a temperature of 30–60°. It is then removed, washed lightly, and squeezed with care. The substantive dyes are applied from a bath containing common salt and sodium carbonate for about three-quarters of an hour, the temperature of the bath being gradually raised during that period to 60°. The presence of soap in the bath favors the manipulation of the material and softens the fiber, but does not prevent the occurrence of streaky dyeings. For a marine



janus and seto dyes, but the diamine<sup>1</sup>, and other<sup>2</sup> basic and direct

blue, none of the substantive dyes is suitable, a much better color being obtainable by the use of janus blue or indophene blue and methyl violet. The sulphide dyes are applied from a cold bath containing, besides the color, sulphide of soda, sodium carbonate, and a small proportion of common salt. The browns and some other shades may be used without danger, but the blues and blacks affect the brilliancy and the handle of the fiber. Colors produced with the aid of the acid dyes, the basic dyes on unmordanted material, and the janus dyes on the cellulose silks, are not fast to water.

1. The direct colors recommended for use comprise: diamine rose BG and BD, fast benzo rose, brilliant geranine G, B and 3B, diamine fast scarlet GB, GG, 4B, benzo fast scarlet GS, 4BS, 5BS, and 8BS, diamine fast red F, diamine brilliant bordeaux R, benzo fast red, thioflavine S, diamine yellow CP, diamine fast yellow FF, diamine orange, oxydiamine red, triazol yellow, chloramine yellow and orange, diamine green B, diamine dark green, benzo green, diamine blue, diamine fast blue, oxydiamine blues, benzo brilliant blue 6B and brilliant azurine.

For drabs and like compound shades: diamine blue black B, oxydiamine black JE, brilliant benzo blue 6B, chloramine yellow M, geranine and pluton brown.

For browns: diamine browns, oxydiamine brown G, diamine catechine G and pluton browns, shading when necessary with yellow or black. When it is required to call into use the basic colors, the artificial silk is mordanted in a bath at 60°, containing 1-4% of tannin, and is worked therein for a short time and left under the liquid for two hours; it is then centrifugally hydroextracted and treated for about half an hour in a 1 or 2% bath of antimony salt.

The basic colors found useful are: Nile blue B, turquoise blue BB and G, methylene blue BB, victoria blue B, new methylene blue N, indazine M, new victoria blue F and R, crystal violet 10B, irisamine G, methyl violet 7B, 2B and R, brilliant rhoduline R, tannin heliotrope, brilliant green, malachite green, fast green; and for shading the greens: thioflavine T and rhoduline yellow 6B.

According to C. Suvern in using the diamine colors for either Chardonnet, cellulose, or viscose silk, soap is added to the dye liquor to soften the material and facilitate the exhaustion of the dye. The amount of liquor for ordinary colors is 30 times the weight of the material. For dark shades and black the proportions vary between 20 and 25 to 1. For bright shades, an addition of 1% of calcined soda and 2% of soap is recommended. The material is treated for one-half hour at 55°. For bright and medium shades, 1% of calcined soda, 2% of soap, and 5% to 10% of Glauber's salts are added. The temperature is brought to 55°; this is slowly raised to 60°, and the material handled for thirty to forty-five minutes. Black can also be dyed at 60°. The dye-bath, particularly for sulphur shades, is not exhausted, and consequently the liquor can be used again to advantage. When using a standing bath, three-quarters of the regular amount of dyestuff is used for light colors and two-thirds for black, along with one-fourth of the original quantity of soap, soda, and Glauber's salts. The colors obtained with basic dyes are developed to some extent by an after-treatment in a solution of acetic acid. Diazotized and developed colors are obtained on artificial silk by the methods used for cotton.

2. Among those especially suitable may be mentioned the basic dyestuffs: auramine O, II, G; brilliant phosphine 5G, 3G; brilliant phosphine G; patent phosphine G, GG, R; chrysoidine G; bisma... brown G, R; safranin G 000, B 000; rhodamine 6G, B, S; diamond magenta; cer... violet 3R, 4B; crystal violet 5BO; ethyl violet; methylene blue G; fast green C, I, JJO; new fast green 2B, 3B; jute black N, V, GN.

The acid dyestuffs particularly suitable for pale shades and for mixtures, are: azo yellow O, I; orange II; rocceline; acid violet 3BN, 4BN, 7B; wool green S; gray R, B, BB.

Among the direct or substantive dyestuffs are: chlorantine yellow JG; chlorantine yellow JJ; cotton yellow CH; chlorantine orange TR; chlorantine orange TRR; direct orange G, R; cotton red 11B 1436; direct safranin, G, B; chlorantine red 4B, 8B; chlorantine pink; chlorantine lilac R, B, BB; direct brown M; cupranil brown G, R, B; chlorantine brown R, B, BB; chlorantine lilac B, BB, R; chlorantine violet B, R; acetylene blue 3R, 6B; acetylene pure blue; direct sky blue, green shade; acetylene sky blue; carbide black S; direct green B695; direct

dyestuffs are probably equally applicable. The dyeing of straw hats and similar heavier material made from artificial ribbons, horse-hair and tubes has recently assumed considerable importance.<sup>1</sup> It has been noted<sup>2</sup> that artificial fibers, which have been treated with aldehydes (formaldehyde) followed by the action of acids or other dehydrating agents, and then washed and dried, have little affinity for dyestuffs. They may, however, be readily dyed if they are first treated with solutions of alkali hydroxides, with or without addition of oxidizing agents, such as hypochlorites. The caustic alkali solution may vary in strength from 1 to 35%, the duration of the action depending on the strength used, but it is preferable to use the more dilute lyes, since the stronger ones cause shrinkage of the fibers unless they are kept under tension during the process.

**Properties of the Artificial Filaments.**<sup>3</sup> The more closely these threads approach in appearance and properties that of natural silk, the more importance will be attached to methods for differentiating between them. Saget and Suvern,<sup>4</sup> A. Herzog<sup>5</sup> and C. Hassack<sup>6</sup> have

gray B, R; dianil yellow 3G, R, 2R, pat.; dianil direct yellow S, oxy-dianil yellow O; aurophenine, G; cresotine yellow G; dianil orange G pat., N; toluylene orange R; brilliant dianil red R; delta purpurine 5B; dianil red R, 4B, 10B; dianil claret red B, G; dianil blue pat., all brands; dianil dark blue R, 3R, pat.; dianil brown 3GO, R, BD; dianil fast brown B; dianil black pat., all brands, particularly CR and CB.

1. A considerable proportion of ladies' light summer hats which appear to command ready sale on account of their beautiful luster and light texture, are, according to E. Wilkinson (Dyer and Calico Printer) made of artificial fibers, especially cuprammonium silk. The hats are not able to withstand rough treatment, and a shower of rain is often sufficient to spoil their appearance. Often they are dyed without regard for fastness, the chief points observed being to produce the mode shades with great exactness in matching and sufficient fastness to the hot pressing which each hat must undergo before it is offered for sale. These "Glanzstoff hats" are dyed—or more properly colored—by simple immersion of the hat in an alcoholic solution of the dyestuff. The basic colors are generally used on account of their bright hues and ready penetration. The most important consideration is to select dyes fast to the temperature of hot pressing in which the hat is given its form. Chrysoidine, which resists the heat when dyed on cotton, turns brown when subjected to the same temperature on artificial silk. Magenta with similar treatment turns a dark, dull violet. Chrysoidine may be replaced by such a color as tannin orange paste, and magenta by the safranines. Artificial silk hats are stiffened with shellac before—not after—dyeing, and may therefore be pressed as soon as dry after dyeing. If not shellacked beforehand, uneven dyeing is apt to result. If in dyeing dark shades the hats "bronze" this may be remedied by wiping with an oily rag. The following dyestuffs are said to be particularly satisfactory for this work: safranin S 150, irisamine, paraphosphine G, tannin orange R paste, brilliant green crystals, new methylene blue 3 R.

2. Fürst Guido Donnersmarch'sche Kunstseiden- u. Acetatwerke, D.R.P. 219848, 1908. For reasons for "Faulty Artificial Silk," see S. Culp, *Färb. Ztg.*, 1910, 21, 141.

3. See W. Massot, *Färb. Ztg.*, 1909, 18, 146, 166, 182; in which the physical and microscopic characters are given, and illustrated by photo-micrographs.

4. *Bull. Soc. d'Industrie Textile*, 1906, 540.

5. Lehne's *Färb. Ztg.*, 1906, 15, 49; *Oest. Chem. Ztg.*, 1906, 9, 166. See "Die Unterabteilung der Kunstseiden- und Künstlichen Seiden," Herzog, 1910, pp. 78; *Lehne's Färb. Ztg.*, 1904, 13, 118. For reactions of artificial silk, *Mon. teint.*, 1904, 48, 56; *Pharm. Centralh.*, 1904, 45, 118.

6. *Oest. Chem. Ztg.*, 1900, No. 1.

studied these differentiations—the latter microscopically—from which sources the following observations may be recorded. Hassock has shown that microscopical examination alone is sufficient to distinguish natural from artificial silk, since all forms of the latter have much coarser filaments, the relative diameters in micromillimeters being:<sup>1</sup>

	Mean. μ	Maximum. μ
Chardonnet silk.....	45 to 60	100
Fismes silk.....	40 to 80	120
Lehner silk.....	60 to 90	135
Pauly silk.....	40 to 50	75
Gelatin silk.....	60 to 80	85
Genuine silk.....	9 to 15	20

Genuine silk can also be immediately differentiated from the artificial by the uniform thickness and roundness of the fiber and with but a few cross stripes, while artificial filaments lack this uniformity, being considerably thicker in some places than in others, as a rule not perfectly round, and often angular, distorted and more or less flattened, especially those Chardonnet silks which have been coagulated in a fluid medium, as distinguished from the filaments produced by "dry spinning," i.e., solidified by exposure to the atmosphere only. The Glanzstoff silk is much more uniform in appearance, approaching more closely a cylinder in structure. Fismes and Walston nitrocellulose silks, as examined by Hassock, resemble Chardonnet filaments under the microscope, Fismes being more conspicuously furrowed lengthwise of the thread. He claims the Chardonnet, Fismes (Du Vivier) and Walston nitrocellulose silks can only be distinguished from each other microscopically by means of the appearance of cross-sections, the latter being readily obtained either by imbedding the filaments in paraffin or gum solution and after hardening, cross-sectioning with a sharp razor, or better, with a microtome. Chardonnet fibers appear somewhat flattened, indented on the surface with minute canals in the interior, and are irregular. Fismes shows for the most part irregular and many-shaped forms, which always contain one or more sharp indentations. The English filaments (Walston) are much more conspicuously flattened and unevenly jagged. The Lehner silk examined by Hassock showed either a broad indented canal, ridged in the middle or at the sides, in which air bubbles are frequently visible, these bubbles being elongated in the longitudinal direction of the filament, indicating the same had been drawn out after spinning and before coagulation. Often could be observed

1. These results are for filaments in a swollen (by water) state. To obtain the air-dry diameters, from 25-33% should be deducted from the figures given.

several heavy, lengthwise lines, usually running in pairs, which cause the edges of the canal-like threads to unite over the canal. Nearly all of the fibers upon sufficient magnification show clear, very closely situated, short stripings or clefts, which could be readily traced to numerous small air bubbles which were contained in the spinning substance and drawn out during the strain after spinning. These bubbles varied from  $3-10\mu$  long and  $1-3\mu$  wide. When these fibers are swollen in Sweitzer's reagent, the fine interior cracks apparently swell into bubbles, inclosing fluid.

Lehner filaments appear jagged, especially in the clefts, and are distinguished by their peculiar cross-section forms, being often in the shape of the letters *V* or *L*, with deep convolutions. The Glanzstoff fibers, which usually consist of from 15-18 filaments, are much more even in structure and shape than the collodion silks, nearly all forms being cylindrical and seldom appreciably flattened, their surface often showing large numbers of finely striated cuts. Air bubbles are infrequently noticed, although sometimes arranged in long chains. In all fibers upon focusing with the medium adjustment extremely delicate radiating lines may be observed in the middle of the fibers, apparently the result of uneven coagulations of the spinning fluid. In many places two obliquely running lines may be detected, undoubtedly caused by the crossing of two threads in the collector. They resemble the crossings in Tussah silk which are caused in the same way. A cross section shows Glanzstoff filaments nearly round, or rounded corners, seldom flattened, and the average diameter far more uniform than the various nitrocellulose silks. The gelatine silks are apparently without distinguishing markings, in cross-section circular, even, with but few bubbles and no striations.

**Polarized Light.** With the exception of threads prepared from gelatin, artificial silk may be distinguished from the natural fiber by its double refraction of light. Höhnel,<sup>1</sup> E. Hanausek,<sup>2</sup> C. Hassock,<sup>3</sup> Chardonnet and others have studied this phenomenon care-

1. F. v. Höhnel, "Die Mikroskopie der technisch verwendeten Faserstoffe," p. 153.

2. "Mittheilungen aus dem Laboratorium f. Warenkunde a. d. Wiener Handelsakademie," 1890.

3. C.R., 1889, 108, 962. Hassock (l.c.) claims that in the dark field of vision of polarization the cellulose silk of Pauly appears brighter in the middle and thickest parts and toward the edges changing to bright yellow, which is a proof of the even thickness and cylindrical form of the threads. Where two threads cross, beautiful steel-blue to purple tones appear, corresponding to the greater thickness of the substance. The collodion silks of Près de Vaux (Chardonnet), Fismes and Walston, seldom show even coloring for any considerable distance, different tones appearing in stripings corresponding to the uneven nature of the cross-sections, in this respect being similar to Tussah silk. At those points where the threads turn their small side toward the eye, green to blue polarization colors

fully, the general consensus of opinion being that although genuine silk possesses the power of refracting light, but to the practiced observer the differences between the natural and artificial fibers are readily apparent. A thread of genuine silk in the polariscope always shows the same relative color dispersion when placed in the same position, the color usually being blue or green when the flattened side is toward the observer.

**Tenacity and Durability** are exceedingly important properties of these fibers, since upon them depend the durability of the fabrics manufactured from them. And it is in these constants that the inferiority as compared with natural silks is most evident. The Bull. of the Imperial Inst. give results of some tests of breaking stresses, given in kilos per square mm.,<sup>1</sup> which are identical with those of Strehlenert and Westergren cited below. R. Bernard<sup>2</sup> records the following figures, in which it will be noted that the process of denitration decreases materially the elasticity and tensile strength of the filaments. This diminution of resistance of the nitrocellulose

	Breaking Strain.	Elongation of Fiber at the moment of rupture.
Nitrocellulose spun (Chardonnet).....	150 gm.	23%
Nitrocellulose denitrated and dried.....	110 "	8%
Nitrocellulose denitrated and wet.....	25 "	....
Nitrocellulose spun (Brommert).....	125 "	28%
Nitrocellulose denitrated and dry.....	115 "	13%
Nitrocellulose denitrated and wet.....	32 "	....
Natural silk.....	300 "	18%

	Breaking Strain. Average of 20 trials.
Skein of bleached cotton (Hauschild) without treatment.....	825
Skein of bleached cotton (Hauschild) without treatment, moistened.....	912
Skein of bleached cotton after hexanitration (by the concentrated sulphonic mixed acids in the cold), dry.....	884
The same after hexanitration, only wet.....	828
The hexanitratd cotton denitrated, dry.....	529
The hexanitratd cotton denitrated, wet.....	206

may usually be seen. Lehner silk shows the most and brightest colors upon polarization, caused by the variation in cross-sections and the varying thickness in the diameter of the filament. In the thicker portions, colors of a higher order appear, as in those places where two threads cross. Cross-sections of artificial silks appear in the dark field in bright colors but different shades on account of the varying thickness of the cross-sections. Those of gelatin silk remain dark.

1. Supplement to the Board of Trade Jour., 1905, 2, 266.

2. Mon. Sci., May, 1905, in Jour. Soc. Dyers and Col., 1905, 21, 167.

caused by denitration, corroborates the opinion of Blondeau, that nitration modifies the structure of the cellulose. Strehlenert and Westergren<sup>1</sup> in a communication to the Chemical Society of Stockholm, submitted the results of a comparative examination of the various types of artificial silk and of the processes by which cellulose is converted into this form. They record their opinion as to the relative advantages of the viscose method, an important factor being that wood pulp is the most suitable raw material for this process, and that it further offers the prospect of working up the waste wood, which in the Scandinavian pulp industry amounts to over 40% of the wood felled.

The following results of determinations of breaking strains are recorded:

	Absolute Breaking Strain in Kilos per sq. mm.		Loss per cent.
	Air Dry.	Wet.	
Natural silk—			
China raw silk.....	53.3	46.7	14.1
French “ “.....	50.4	40.9	18.8
“ “ silk, boiled off.....	25.5	13.6	46.7
“ “ dyed red and weighed.....	20.0	15.6	22
“ “ blue black, 110% weighting.....	12.1	8.0	33.9
“ “ black 140% weighting.....	7.9	6.3	20.3
“ “ “ 500% weighting.....	2.2	.....	.....
Collodion silks—			
Chardonnnet, undyed.....	14.7	1.7	89.6
Lehner, undyed.....	17.1	4.3	74.8
Strehlenert, undyed.....	15.9	3.6	77.1
Pauly, undyed.....	19.1	3.2	72.7
Cross and Stern, viscose.....	11.4	3.5	70.0
Cross and Stern, latest viscose “silk”.....	21.5	3.5	81.0
Cotton yarn.....	11.5	18.6	83.0

Hassock determined the tenacity by means of breaking-strain tests<sup>2</sup>

1. Chem. Zeit. 1901, **25**, 1900; abst. J.S.C.I., 1902, **21**, 113; Brounert (Bull. Soc. Ind., Mulh. 1900) in an isolated test, found 77% loss in strength on wetting Chardonnnet silk. J. Gebauer (F.P. 403264, 1909) seeks to improve the elasticity and resistance to water of artificial silk by producing a thread of artificial silk and caoutchouc, the latter ingredient being subsequently vulcanized. A solution of caoutchouc may be added to the spinning solution, or the thread or tissue of artificial silk may be passed through the caoutchouc solution. Vulcanization is carried out in the ordinary way with sulphur chloride. (See S. Torii, F.P. 407345, 1909.)

2. The method used was to place pieces of genuine silk and artificial silk filaments in a tensile-strength machine in such a manner that a free thread of an arbitrary but always the same length (in this instance 3.93 inches) lay between the fastening screws when the filaments were pulled out taut but not stretched. The tension was gradually increased until the moment of breaking when the elongation

the results being several times repeated, the arithmetical mean of which are appended below:

Genuine silk (Piemont-Organin).....	21.6 per cent.
Chardonnet silk from Près de Vaux.....	8.0 "
Collodion silk from Fismes.....	11.6 "
Collodion silk from Walston.....	7.9 "
Lehner silk.....	7.5 "
Pauly's cellulose silk.....	12.5 "
Gelatin silk.....	3.8 "

In order to compare the results directly with genuine silk (the sample being of medium tenacity and the titer 22-24 denier), the calculations are recorded in the following table, the relative tearing resistance being calculated in the last column on the basis of a unit titer of 100 denier.

Quality.	Denier.	Breaking Strain in gm.	Do. per Denier in gm.	Elasticity, per cent. (Genuine Silk = 100.)
Genuine silk.....	23	57.5	2.5	21.6
Chardonnet silk.....	80	74.2	0.93	8.0
Fismes.....	100	71.7	0.71	11.6
Walston.....	120	151.4	1.26	7.9
Lehner.....	120	171.8	1.43	7.5
Pauly.....	120	197.6	1.64	12.5
Gelatin.....	100	63.0	0.63	3.8

Recent figures given by the testing department of the Manchester Chamber of Commerce show the following results:

Yarn.	Dry Strength.	Wet Strength.	Loss Per Cent.
Glanzstoff.....	92.5	31	66
Cellulo silk.....	75.5	33	56

According to these figures the Glanzstoff product now loses 17% less "on wetting" than in 1901. The Cellulo silk product loses still less. The present-day strength (dry) is given by Cross and Bevan at 1.0-1.4 gm. per denier, against 2.0-2.5 gm. for real silk.

W. Dreaper reports having received a sample of 25 denier artificial thread containing 60 filaments and having a breaking strain of 58.5 gm., indicating a breaking strain of 2.3 gm. per denier, which is not inferior to some silks. He has given the following figures, which indicate for the same make of silk an important increase in strength

and weight required to break the filament were carefully noted. After each test the fiber was examined under the microscope and the individual filaments composing it counted, in order to express the results per unit filament.

for the finer sizes per unit weight of thread (denier) and with it a "decrease in elongation before breaking," the latter figure not necessarily indicating that the elasticity is decreased:

Size in Deniers of Artificial Filament.	Per cent. Elongation Before Breaking.	Breaking Strain per Denier in Grams.
20	9.0	...
40	10.5	2.7
60	12.5	1.7
80	14.	1.5
100	15.	1.3
120	16.	1.2
140	16.5	1.1

**Moisture.** The investigations of Hassock on the moisture and hygroscopicity of artificial filaments are appended below, the first table giving the results of the determination of moisture calculated to 100 gm. dry substance, as follows:

	Moisture in per cent.
Indian raw silk.....	8.71
Près de Vaux silk (Chardonnnet silk).....	11.11
Fismes silk.....	10.92
Walston silk.....	11.32
Lehner silk from Glattbrugg.....	11.45
Pauly cellulose silk.....	9.20
Gelatin silk.....	13.98

The hygroscopicity was determined by the difference in weight between artificially dried samples and the same sample after exposure to an atmosphere saturated with steam for a period of twenty-four hours.<sup>1</sup> The percentage absorption of water was as follows:

Italian raw silk.....	20.11
Près de Vaux silk.....	27.46
Fismes silk.....	27.12
Walston silk.....	28.94
Lehner silk from Glattbrugg.....	26.45
Cellulose silk.....	23.08
Gelatin silk.....	45.56

1. The Textile Ztg. (1904, No. 35) states that at the Elberfeld-Barmen silk conditioning establishment, artificial silk is found to be as hygroscopic as ordinary silk. As the result of several hundred tests the amount of moisture was found to vary between 9.30-12.99%, giving an average of 11.30%. Having been granted permission by the government, this conditioning establishment now undertakes the valuation of artificial silks on the basis of 11% moisture. Besides moisture, the net weight, counts, twist, elasticity, and tensile strength, are determined, and especial attention is devoted to the question of inflammability, since in Germany users of artificial silk made from nitrocellulose have to pay an unjustifiably increased premium to the private insurance companies. Undenitrated artificial silk consists of only 2-3.5% moisture. Herzog (Färb. Ztg. 1895, 6, 49) found that in a room of average dryness, dry artificial silk absorbed in two hours 16% of moisture.



Genuine silk.....	100
Chardonnet silk.....	44
Vivier silk.....	29
Pauly silk.....	45 to 50
Lehner silk.....	68

Nature of Yarn.	Per cent.
Pauly make (Cuprammonium).....	.13
Chardonnet (Nitrocellulose) French.....	.15
“ “ German.....	.16
Lehner “.....	.07
Nitrocellulose.....	9.15 to 14.14

Silk.....	Brown coloration.
Tussah silk.....	Intense brown.
Chardonnnet and Lehner (Nitrocellulose).....	Intense blue.
Pauly, Viscose or Yarmouth silks.....	No reaction.

The defects which may be said to interfere with the universal use of artificial filaments for all the uses to which natural silk is put is, according to W. Dreaper<sup>1</sup> comprehended in the following:

1. Jour. Soc. Dyers. Col., 1907, 23, 7.

(2) The filaments which make up these threads are much larger than the real silk ones.

(3) Strength, and elasticity are not satisfactory, especially the latter.

(4) The loss of strength on wetting is excessive.

(5) The lack of covering power reduces the value of the product.

The combined effect of these defects removes these products outside the limits of ordinary dress materials. On the other hand, the harsh feel is not considered a defect in the manufacture of braids, etc.

**Chemical Properties of the Artificial Fibers.** C. Suvern (l.c.) and C. C. Hassock (l.c.) have made exhaustive comparisons of the deportment of natural and artificial silks with various reagents, in attempts to differentiate these two classes of fibers by means of well-defined chemical reactions. China and Tussah natural silks and the artificial filaments prepared according to the methods of Chardonnet at Besançon and Spreitenbach, Lehner's product, and the filaments produced by the cupranmonium methods of Pauly, Bronnert, Fremery and Urban were compared under similar conditions, that small differences might be more apparent. As these investigations form the most complete research on this subject so far appearing, their composite results are given somewhat in detail.

(1) *Potassium Hydroxide* solution of maximum concentration dissolves the natural silks, Tussah less readily, but completely on boiling, the cellulose "silks" becoming discolored, gelatinized, and transparent, but incompletely dissolving except upon long boiling. Lehner and Pauly filaments were most resistant.

(2) *Potassium Hydroxide* 40% solution completely dissolves China silk at 65-85°, Tussah being more resistant, swelling considerably at 75°, and passing completely into solution at 100-120°. The cellulose filaments began to swell at the room temperature, but resisted the influence of the alkali for considerable time. Pauly silk fast discolored but showed no swelling, being least affected by this treatment. Chardonnet Besançon was most susceptible to treatment with 40% KOH solution.

(3) *Zinc Chloride Solution* 60% (not 40%). The samples were all shaken with zinc chloride solution in test tubes, and heated in a bath of concentrated sulphuric acid. China silk was readily affected, Tussah less easily, the artificial silks offering more resistance at 100°, especially the Pauly, which dissolved only at 180°, the collodion products passing into solution at 140-145°. No violent foaming of the silks was noted, as stated in the literature. With this method of examination very prominent differences appeared, Tussah and the

collodion silks forming one group dissolving at 145°, as against China silk at 120°.

(4) *Alkaline Copper* solution in glycerol prepared by dissolving 10 gm. copper sulphate crystals in 100 cc. water, adding 5 gm. glycerol and 10 cc. of 40% KOH aqueous solution. The precipitate of cupric hydroxide first formed with the alkali just redissolved upon addition of 10 cc. total KOH solution. In this solution China silk dissolved while the others were inappreciably affected, even at the temperature of boiling.

(5) *Ammoniacal Nickel oxide* solution was obtained by saturating nickel sulphate with an alkaline hydroxide, washing the nickel hydroxide and redissolving the precipitate in the minimum of ammonia. China silk readily dissolved at room temperature, and completely on boiling, the other samples being unaffected.

(6) *Cuprammonium Solution*, prepared by dissolving well-washed cupric hydroxide in 24% ammonia. In this reagent the China silk only was dissolved, the others undergoing no appreciable change.

(7) *Fehling's solution*. Natural silks dissolved clearly, Tussah with difficulty, the artificial fibers being unaffected.

(8) *Concentrated Nitric Acid* decomposed China silk in the cold, Tussah still more readily, the artificial silks remaining unchanged for a considerable time. All dissolved on boiling, the Pauly with a dark yellow color.

(9) *Chromic Acid* solution 4% and 20%. The weaker solution had no apparent effect on any, even at boiling. 20% solution at boiling dissolved all but Tussah, the latter retaining a loose thread-like structure.

(10) *Millon's Reagent*, at boiling, both natural silks gave a violet color, while the four artificial silks showed no change.

(11) *Iodine* in potassium iodide solution. The samples were moistened with water and a drop of the reagent added. China silk being colored a deep brown, Tussah a pale brown, the collodion silks first turning brown and then blue. Pauly filaments showed no change.

(12) *Diphenylamine Sulphate*. Diphenylamine was dissolved in concentrated sulphuric acid, 1-2 cc. of the solution poured on a watch-glass with white background, and short threads stirred in with a glass rod. China silk showed light brown, Tussah heavy brown, Besangon, Spreitenbach and Lehner showed dark blue with a strong nitro reaction, while Pauly filaments gave no change.

(13) *Brucine Sulphate*, in concentrated sulphuric acid gave but slight browning with the natural silks, the nitro-silks a deep red color, Pauly silk no change.

(15) *Determination of Moisture.* 5 gm. of each kind when dried at 99°, until no further loss in weight occurred gave the following results:

China.....	7.97%	water.
Tussah.....	8.26%	“
Art. silk Chardonnnet Besançon.....	10.37%	“
“ “ Spreitenbach.....	11.17%	“
“ Lehner.....	10.71%	“
“ Pauly.....	10.04%	“

	China gm.	Tussah gm.	Chardon- net B. gm.	Chardon- net S. gm.	Lehner gm.	Pauly gm.
After 15 minutes. ....	0.0052	0.0145	0.0091	0.0066	0.0071	0.0120
“ 1½ hours. ....	0.0098	0.0367	0.0320	0.0334	0.0314	0.0400
“ 17 “ ....	0.0520	0.1546	0.1394	0.1490	0.1572	0.1910
“ 24 “ ....	0.0452	0.0442	0.1015	0.0995	0.1026	0.1040
Total after about 43 hrs. .	0.1122	0.2500	0.2820	0.2885	0.2983	0.3470

(17) *Behavior on heating to 200°.* After heating the dried samples to 200° for two hours, China silk was considerably browned, Tussah apparently suffering no change. The nitro silks were carbonized to blue-black coals, but retained their thread-like form. Paddy silk appeared bright yellow and was not charred. The loss in weight by this treatment is as follows.

	Grams.	Per cent.
China decreased about.....	0.1592	equal to 3.18
Tussah " " .....	0.1475	" " 2.95
Chardonnnet Besangon decreased about.....	1.6640	" " 33.28
Spreitenbach " " .....	1.7065	" " 34.13
Lehner decreased about.....	1.3278	" " 26.56
Pauly " " .....	0.0808	" " 1.61

China.....	0.95	%	Ash.
Tussah.....	1.65	%	“
Chardonnet Besançon.....	1.60	%	“
“ Spreitenbach.....	1.03	%	“
Lehner.....	1.43	%	“
Pauly.....	0.096	%	“

The ash of Pauly silk is remarkably low.

(19) *Nitrogen* determinations resulted in the following figures:

China.....	16.60%	Nitrogen.
Tussah.....	16.79%	"
Chardonnet Besançon.....	0.15%	"
" Spreitenbach.....	0.05%	"
Lehner.....	0.07%	"
Pauly.....	0.13%	"

According to C. Schwalbe<sup>1</sup> the methods of Süvern just enumerated for testing artificial silks are not altogether trustworthy. As a means of distinguishing between Chardonnet, Pauly, and viscose silks, Fehling's solution and a solution containing zinc chloride and iodine are recommended. If 0.2 gm. of each of these silks be treated in separate test-tubes with 2 cc. of Fehling's solution, the Chardonnet silk, owing to its reducing action, imparts a green color to the liquid, while the liquid in the other two tubes remains blue. To distinguish between Pauly and viscose silks, equal quantities of these are treated with a solution containing 20 gm. of zinc chloride, 2 gm. of potassium iodide and 0.1 gm. of iodine dissolved in 15 gm. of water. The silks are then washed with water. Both silks become at first somewhat colored, but whereas the viscose silk keeps its color (bluish-green) for a long time, the Pauly silk quickly loses its (brown) color during the washing.

A simple way to determine the presence of artificial silk in a fabric without the use of reagents, it is said, is to submit a weighed cutting of the fabric to a temperature of 200° for ten minutes. On being subsequently rubbed, any artificial silk present is said to drop out as dust, the percentage of which can be ascertained by reweighing.<sup>2</sup>

According to Coppetti<sup>3</sup> the usual tests for distinguishing between natural and artificial silks frequently fail when the fabrics are weighted and dyed, and there are very few methods available for stripping the loading and dyestuff from the silk without destroying the fiber. The author has found that hydrofluoric acid is an excellent stripping agent, which readily removes the most refractory of the mineral loadings commonly employed. The fabric is steeped in hydrofluoric acid of the ordinary commercial strength for five to ten minutes; it is then washed and heated in a solution of soap to the boiling point. It is washed again and placed in a 5% solution of hydrochloric acid, with which it is boiled. Next it is bleached in a solution of sodium

1. *Färb. Ztg.*, 1907, 18, 237; *Wochbl. Papierfabr.*, 1908, 38, 3913. See Schwalbe, *F.P.* 410460, 1909.

2. This test presumably applies to the nitrocellulose silks, rather than the cuprammonium or viscose silks.

3. *Ann. Chim. analyt.*, 1909, 14, 47.

hypochlorite, again acidified, then washed and dried. An alternative method of bleaching, according to the nature and intensity of the dyestuff, consists in treating the fabric with a permanganate solution, followed by sulphurous acid. In this way the fibers are obtained practically free from mineral weighting and coloring matters, and the usual tests for the nature of the silk can be applied. When the fibers are sufficiently colorless, nitric acid is the best reagent for distinguishing between the silks of animal and those of vegetable origin; but if the residual color is such as to mask the yellow stain produced by nitric acid, the fibers should be gently warmed on a glass slide with a 20% solution of potassium hydroxide, which dissolves the natural silks and the artificial silks which are composed of gelatin.

W. Minajeff<sup>1</sup> has examined microscopically the dyed fibers of cotton and "Glanzstoff" from which are drawn the following conclusions. The cuticula of the cotton fiber has no influence on the dyeing of that fiber, and the layer-like structure of the fiber walls is also of no substantial importance. The greater density of the cotton fiber compared with that of "Glanzstoff" and also the greater difficulty of penetration by liquids, are of greater importance. The thickness of the fiber has also a special effect on the dyeing of the fiber. The canal of the fiber is of some importance; but its effect is small, since it has been found that on dyeing cotton with mordant dyestuffs, only small aggregates of the color-lake are found in the canal, and that these only exist about the broken ends of the fibers. More importance is attached to the physical properties of the fibers, i.e., rather to the thickness, density, and capillarity of the fiber substance than to the inner structure of the fiber.

**Uses of Artificial Silk.** In addition to the fields of usefulness already mentioned, it is finding increased employment in lace manufacture, more especially for embroidery lace and the heavier laces and braids used on hats. On the Lever machines it is more difficult to work than cotton or silk filaments, owing to the chafing through the intricate parts of the machine. The objection that the artificial filaments are unable to stand rain or repeated wetting is partially overcome by blending with the natural article. It is also said that by combining a nitrocellulose and silk filament the former adds a very desirable brilliancy, and the latter contributes strength, which adds to its value in laces, passementerie, mousselines, ribbons, gauzes, and trimming material. A new article called chifolinceis, a species

1. Z. Färben-Ind., 1908, 7, 63, 81, 236.

of goods manufactured from crin de Chardonnet, is used very largely in the trimming of ladies' hats. The coarseness of the artificial filaments prevents their being used for the production of fine soft textures, such as velvets, duchess, foulards, bengalines and a number of other silk textures. For figuring upholsteries that are not subjected to severe abrasive wear, it has been extensively adopted. On account of the lack of durability of fabrics made of artificial silk alone, pure silk or another fiber is usually woven in the textile as the warp, while artificial silk is used for the woof. At present there is a demand<sup>1</sup> in the United States for a sort of heavy tulle made of ovale of 500 deniers of artificial silk coming from France. This material is used on dresses as a trimming over a foundation of taffetas or satin.

**The World's Output of Artificial Silk** has recently been stated as 3,500,000 k. per annum, and is rapidly increasing.<sup>2</sup> Comparing this with 1,700,000 k. in 1906, and 600,000 k. in 1896, the increase indicated is nearly 600% in thirteen years. The nitrocellulose silks come first with an estimated output of between 1,500,000 and 1,800,000 k.; the copper ammonia process in the neighborhood of 1,250,000 k.; viscose silk about 600,000 k. and acetate silk comparatively little. The production of artificial silk<sup>3</sup> in Germany rose during 1908 to about 1,200,000 k.; and the demand has exceeded this, 300,000 k. being imported from Switzerland and Belgium. The value of the silk consumed amounted to approximately \$5,000,000. The total production of the world appears to be about 4,000,000 k. Of this quantity the nitrocellulose process, worked in Germany by the Vereinigte Kunstseidefabriken of Frankfort, continues to represent the greater part with about 2,000,000 k., and during 1909 has increased this to an enormous extent; while the ammoniacal copper oxide process of the Vereinigte Glanzstoff-Fabriken of Elberfeld accounts for 1,450,000 k.

The viscose process, which for the first time produced on a large scale in 1907, rose rapidly in importance owing to the fineness and brilliancy of its thread, and represents about 600,000 k. The following table gives the results of the various companies working the nitrocellulose process in 1908:

1. According to U.S. Consul J. Covert of Lyons, France, U.S. Daily Consular and Trade Report 1909, 3431, 11.

2. A. Colin (Rev. gén. Chim., 1909, 12, 40) gives the 1909 production at four million k. R. Schwarr (Neue Freie Presse, Vienna, Jan. 5, 1909) estimates there are at present (1909) in Europe, 30 producing artificial silk factories, producing in 1907, 3,300,000 k., of which 1,500,000 were nitrocellulose silk, 1,300,000 "Glanzstoff," and 500,000 viscose silk.

3. Chem. Trade Jour., 1910, Jan. 8.

## Nitrocellulose (Chardonnet) Process

Companies.	Production in kilos.	Gross Profit.	Dividend, per cent.	Capital.	Sinking Fund.	Reserve.	Total Reserves.
Chardon-Besançon .	700,000	1,151,504fr.	60	900,000fr.	50,000fr.	.....	3,988,560fr.
Artificielle Tubize . . . .	500,000	2,294,575fr.	50	1,010,000fr.	516,774fr.	350,000fr.	920,000fr.
Unst. A.-G. . . .	425,000	720,968M.	10	365,000M.	245,703M.	20,000M.	2,629,130M.
nkfort . . . . .	250,000	790,000Cr.	..	.....	276,000Cr.	.....	.....

The last company had a debt to liquidate from the previous year 34,599 Cr. The Societa Italiana della Sete Artificiale of Pavia, adopting the same process, had a loss of 30,736 lire, and the Chardonnet Company of Paris entered into liquidation. The Tubize Company has announced an enlargement of business. The ammonia-copper oxide process, judging from the profits of the companies adopting it, would seem to yield more uniform results, as the following shows:

Company.	Production in kilos.	Gross Profit.	Dividend, per cent.	Capital.	Sinking Fund.	Reserve.	Total Reserves.
Glanzstoff-Elberfeld .	800,000	2,876,889M.	40	1,000,000M.	1,059,437M.	550,000M.	3,962,323M.
ster, Glstf. . . .	250,000	772,680M.	10	250,000M.	324,614M.	68,242M.	15,152M.
Polten . . . . .	200,000	511,622fr.	17	806,802fr.	142,262fr.	20,297fr.	86,543fr.
rtif. Paris . . . .	150,000	380,389fr.	6	149,351fr.	137,953 fr.	31,121fr.	31,121fr.

The German and Austrian companies have now considerably extended their works.

As a consequence of the British Patents Act the Vereinigte Glanzstoff-fabriken have been obliged to form a company, the British Glanzstoff Manufacturing Company, Ltd., Liverpool, with a capital of £125,000, which expects to turn out from its factory at Flint 250,000 kilos annually.

There are no figures of importance available regarding the viscose process, as the principal manufacturers exploiting this method, the Nobel Donnersmarck'schen Kunstseiden und Acetatwerke of Sydswede, being a private firm, do not publish a report. Their production, however, is estimated at about 120,000 k. In England Tait & Co. of Coventry, are said to have produced 375,000 k. in 1908, making a profit of £16,968.

The production of natural silk for 1908 of the 21 European spinning houses totaled 51,445,000 lb. as against 34,929,400 lb. in



1896-98, a net gain of but 30% in a decade. This included the three great producing centers—Europe, the Levant, and the Far East. The increase in Europe during this period is but 20% as compared with 50% in the Far East, and 100% for Asia Minor. This last increase is said to be primarily due to the efforts of the Silk Institute at Broussa, and the consequent introduction of scientific methods, especially in investigations of the entomology of the insects attacking the silk-worm larva. In France the production of cocoons has not increased for some years past, notwithstanding the fact that the French Government expends annually approximately \$750,000 in state bounties to encourage their propagation.

In 1906, 227 spinning mills turned out 1,732,018 lb. of silk in France, and 1908 the amount had not increased.

The fact that artificial filaments, on account of their decreased tenderness and frangibility in the wet state, have not come into general competition with the filament from the silk worm, undoubtedly accounts for the fact that the phenomenal rise and expansion of the artificial silk industry has had no appreciable effect on the world's markets for natural silk. And as the ramifications of these artificial filaments are expanding, and new uses are continually being found, it very clearly appears that the consumption of artificial filaments must be very much larger than at the present day in order to influence to a detrimental extent the world's production of natural silk.<sup>1</sup>

1. The following information is taken from an article by J. Matthews in *Textile Colorist*, 27, 322:

*Société bisontine de Soie Chardonnnet*, founded in the year 1890 with a capital of \$400,000, its actual daily production being 1,500 k. (3,300 lb.).

*Société de Tubize, system Chardonnnet*, founded in the year 1890 with a capital of \$200,000; its actual daily production amounting to 1,600 k. (3,520 lb.).

*Soie artificielle de Givet*, founded in the year 1903 with a capital of \$300,000; its daily production being 200 k. (660 lb.).

*Vereinigte Kunstseide-fabriken* at Frankfort-on-the-Main, Germany, founded in 1900 with a capital of 2,500,000 marks; its daily production is now over 2,000 k. (4,400 lb.).

*Vereinigte Glanzstoff-fabriken*, at Elberfeld, Germany, established in 1899 with a capital of 2,000,000 marks; the daily production of silk by this company in its several factories now amounts to over 1,200 k. (2,640 lb.).

*Société française de la Viscose* was established in 1904 with a capital of \$440,000; its factory has a projected daily production of 500 k. (1,100 lbs.).

*Société française de la Viscose*, with a capital of \$848,000, and a similar projected production of silk.

*Société italienne de la Viscose*, with a capital of \$600,000, and a similar projected production.

*Société russe de la Viscose*, with a capital of \$800,000 and a similar projected production. These last four companies operate under the same patents and manufacture the silk from viscose. There is also a company operating under patents in England.

There is also a company established for the manufacture of artificial silk at Obourg, Belgium; it has a capitalization of \$200,000, and a projected daily production of 500 k. (1,100 lbs.). Another company at Nivonne, France, with a capital of \$200,000, also proposes to manufacture 500 k. of silk per day. There

is another French company of J. D. Ramel, with a capital of \$500,000, but which does not yet produce any silk. A Russian branch of the Tubize factory is also established with a capital of \$1,000,000.

In addition to the above there are four other French companies, as follows: The *Soie de Beaulieu* with a capital of \$400,000; the *Soie Vallesle* at Lyons, with a capital of \$300,000; the *Soie artificielle d'Izieux*, with a capital of \$400,000; and the *Textiles Lyonnaise*, with a capital of \$160,000. None of these companies is as yet an actual producer of silk.

In addition to the companies mentioned in the foregoing summary there are several others located in Germany, Switzerland, and England, from which statistics are not available.

The *Compagnie de la Soie de Beaulieu* was organized in Paris in July, 1904. It is capitalized at 2,000,000 francs. Its process of manufacture is very similar to that employed by the Chardonnet company.

The *Société la Soie artificielle* is another French company, capitalized at 1,500,000 francs. It was organized in 1902, and acquired the patents held by the *Compagnie française de la Soie parisienne*. The process by which it operates depends on the formation of filaments from solutions of cellulose in ammoniacal copper oxide. The factory of the company is located at Givet; hence the product is known as "Givet silk." A branch of this company is the *Soie artificielle d'Izieux* at Lyons; it has a factory at Izieux near St. Charmond.

The *Textiles Lyonnaise* company deals in other things besides artificial silk, but takes the entire output of the *Société A. Lumière et Fils*.

The *Société de la Soie artificielle l'alelle* at Lyons was organized in 1904 with a capital of 1,500,000 francs.

The first German company for the manufacture of artificial silk was the *Vereinigte Glanzstoff-fabriken*, established in September, 1890, at Aix-la-Chapelle. It was formed for the commercial exploitation of "Glanzstoff." This is the same company which transferred its French patents to the *Soie parisienne* company; this latter company was absorbed by the *Soie artificielle d'Izieux* company, which in turn transferred to the Lyonnaise factory of . . . to manufacture the product under the name of "Soie artificielle d'Izieux." This first German company started with a capital of 2,000,000 marks, one-half of which served to pay for the patent rights. The company now operates two factories, one at Oberbrück in Westphalia and the other at Niederworsmiller, near Mulhouse.

The second German company to be formed was the *Vereinigte Kunstseide-fabriken*, established at Frankfort in February, 1900. It commenced with a capital of 2,500,000 marks, and its work is under the direction of Becker and Lehner. The company now operates four factories: One at Spreitenbach, which had previously been operated by Lehner, whose process of manufacture is a modification of the Chardonnet method; a second at Glattbrugg; a third at Bobingen; and a fourth at Kestlerbach.

The *Vereinigte Glanzstoff-fabriken* at Oberbrück, Germany, has been operating its factory during the past year both night and day without interruption; over 1,700 workmen are employed at this factory.

The introduction of the manufacture of artificial silk into Italy has apparently caused considerable concern among several of the Italian silk manufacturers; so much so, in fact, that the government has been petitioned to prevent the sale of the artificial fiber under the name of silk, as it is feared the natural silk industry will suffer thereby.

The establishment of a factory for the manufacture of artificial silk was under consideration at Wilanow, near Tamashow, in Russian Poland. Owing to the recent political troubles there, however, it has been decided to locate the factory in the province of Posen, or German Poland.

